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# Exploratory Research on Novel Coal Liquefaction Concept

## Task 2 - Evaluation of Process Steps Topical Report

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TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

TABLE OF CONTENTS (Continued)



LIST OF TABLES

LIST OF TABLES (Continued)

LIST OF FIGURES

LIST OF FIGURES (Continued)



APPENDICES

# EXECUTIVE SUMMARY

## PROGRAM DESCRIPTION

A novel direct coal liquefaction technology is being investigated in a program being conducted by CONSOL Inc. with the University of Kentucky, Center for Applied Energy Research and LDP Associates under DOE Contract DE-AC22-95PC95050. The novel concept consists of a new approach to coal liquefaction chemistry which avoids some of the inherent limitations of current high-temperature thermal liquefaction processes. The chemistry employed is based on hydride ion donation to solubilize coal at temperatures (350-400 °C) significantly lower than those typically used in conventional coal liquefaction.

The process concept being explored consists of two reaction stages. In the first stage, the coal is solubilized by hydride ion donation. In the second, the products are catalytically upgraded to acceptable refinery feedstocks. The program explores not only the initial solubilization step, but integration of the subsequent processing steps, including an interstage solids-separation step, to produce distillate products. A unique feature of the process concept is that many of the individual reaction steps can be decoupled, because little recycle around the liquefaction system is expected. This allows for considerable latitude in the process design. Furthermore, this has allowed for each key element in the process to be explored independently in laboratory work conducted under Task 2 of the program.

A systematic study was conducted in 45 mL microautoclaves to determine the range of low-severity first-stage reaction conditions which produce high coal conversions. Variables tested were coal rank, residence time, reaction temperature, solvent type, solvent-to-coal ratios, hydride ion sources, hydride ion reagent-to-coal ratios, and total reactor charge size. Scale-up of the first-stage reaction to a one-liter stirred autoclave was successfully accomplished.

Filtration was tested for the removal of unreacted coal and mineral matter from the liquefaction process. The preliminary conceptual design, which forms the basis for Task 2 work, places a filter directly following the first-stage solubilization reactor and ahead of a second-stage catalytic upgrading step. The successful demonstration of filtration of the first-stage product confirms the viability of filtration as the primary solids-separation technique. Placement of the filter interstage between the solubilization and catalytic upgrading steps appears to be feasible.

Catalytic hydroprocessing was used to upgrade the first-stage filtrate. Preliminary upgrading studies were performed using a conventional two-stage liquefaction distillation resid to establish conditions and select an appropriate catalyst. Subsequent work was done with 566°C$^+$ filtrate resids of the first-stage products.

The first portion of an engineering and economic evaluation has been conducted concurrently with experimental work throughout Task 2. This continuing evaluation will guide the studies to be conducted under Tasks 3 and 4.

## KEY FINDINGS AND ACCOMPLISHMENTS

### SOLUBILIZATION AND PRODUCT CHARACTERIZATION

- Low-severity reaction conditions ($\leq$400°C, $\leq$60 min) were determined for which high coal conversions (>90wt%) to soluble products were obtained with five different coals of three different coal ranks.

- The effects on coal conversion of temperature, residence time, coal rank, hydride ion-to-coal ratio, solvent type, and total reactor charge size were explored.

- Some solvent is necessary to achieve high coal conversion although it does not have to be a hydrogen donating solvent. The aromaticity of the solvent appears to be important for obtaining high coal conversions at the lowest severity reaction conditions.

- The coal-derived soluble products are enriched in hydrogen and depleted in oxygen relative to the starting coal.

- The hydride ion reaction system was compared to the CO/$H_2O$ and CO/methanol reaction systems. CO gave improved coal conversion over thermal reaction, but gave coal conversions much poorer than with the molar equivalent amount of hydride ion reagent. Coal conversions with CO/methanol gave conversions intermediate to those obtained with CO and hydride ion reagent.

- Experiments were successfully scaled up from 45 mL microautoclaves to a one-liter stirred autoclave.

- A hot transfer of first-stage products from the one-liter autoclave to a contiguous receiver vessel was successfully completed.

## FILTRATION

- Hot pressure filtration effectively removed solids from first-stage products. Experimentally determined filtration rates of first-stage products were found to be very fast (in some cases, >300 $kg/m^2 \cdot hr$) and filter cake solids contents are as high as 90%.

- The rates of filtration achieved at around 300 °C and 0.3 MPa with feedstocks made from several coals (bituminous, subbituminous and lignite) indicate the filtration in a commercial plant would contribute 40¢ to the cost of a barrel of oil.

- The reaction product solids are capable of bridging across relatively large orifices (e.g., 100 µm x 500 µm). This would enable a coarse and relatively robust material to be used as the filter screen.

- The optimum distillate solvent to coal ratio for filtration was determined to be around 1:1 or 1.5:1, depending on the coal, the extraction conditions (severity), and the filtration temperature.

- The viscosity determinations on filtrates, and filtrates concentrated by vacuum distillation, indicate that the majority of the distillate solvent could be recovered before upgrading and still give a pumpable fluid at 300 °C

- About 2% of the coal (other than ash and IOM) is discarded with the filter cake by omitting a wash stage in the filtration cycle; this would drop the effective first-stage conversion from 92% to 90%. This drop is small compared with other solid-liquid separation methods.

## CATALYTIC UPGRADING

- At 440 °C, filtered first-stage products gave significantly higher resid conversions than a conventional two-stage liquefaction deashed resid (DAR) from Wilsonville Run 258 Hydrogen consumption per unit resid conversion for filtrate was lower than for the DAR. Lignite-derived filtrates gave the highest resid conversion to distillate products.

- A $2^3$ factorial experiment was completed to delineate the catalytic upgrading characteristics and behavior of the hydride ion liquefaction product. Three factors were evaluated in the study: reaction time, reaction temperature, and catalyst concentration.

- Linear models were developed to mathematically describe six results of the catalytic upgrading experiments: 566 °C$^+$ resid conversion, $C_1$-$C_3$ gas yield, $C_4$+ gas yield, $CO_x$ gas yield, total gas yield and $H_2$ consumption. Correlation coefficients for two of the key results, resid conversion, and light hydrocarbon gas yield, were 0.97 and 0.98, respectively.

- $C_1$-$C_3$ gas yield and hydrogen consumption per unit of 566 °C$^+$ resid conversion are dependent on temperature and catalyst concentration. Improved hydrogen utilization efficiency can be achieved at low reaction temperatures and longer residence times.

- Catalytic upgrading experiments with concentrated resid feed resulted in high resid conversion and high efficiency. This indicates that a low vehicle solvent-to-resid ratio in the feed to the catalytic upgrading process may be advantageous.

- A dispersed catalyst (Molyvan L) was selected and reaction conditions (440°C, 60 min) were defined for use in subsequent larger scale testing.

- Thermal pretreatment of catalysts is not required for good catalytic activity.

ENGINEERING AND ECONOMIC EVALUATION

- Technical and economic assessments of the experimental data were developed in order to guide the experimental program concurrent with its execution.

- A literature and patent survey was completed on hydride ion reagent synthesis. The survey was conducted to identify potential transferagents and their respective production methods, assess the cost of production of potential transfer agents, and identify areas requiring further investigation.

- The merit of the tested novel concept was assessed by comparing the initial results of this program with the results achieved by current, state-of-the-artprocessing technologies.

- The preliminary technoeconomic evaluation shows that a high distillate and low $C_1$-$C_3$ yield can be obtained with the novel process concept. This indicates the potential technical merit of the hydride ion-donation approach.

- The economic impact of the preliminary estimate of hydride ion reagent “A” consumption is significant. If the hydride ion reagent "A" consumption rate were 0.5 lb/lb of MF coal fed to liquefaction, the estimated cost of using hydride ion reagent "A", exclusive of feedstock costs, would be approximately $15 per barrel of product. The importance of the reagent consumption to the economics of the process indicates the need to ascertain the true reagent “A” consumption rate in the first-stage operation and to develop ways in which similar overall results can be achieved by using a lower amount of reagent “A”, perhaps in combination with other active, but less expensive, solubilizing agents, such as carbon monoxide and methanol.

## SUMMARY ASSESSMENT AND FORECAST

High coal conversions obtained in the first-stage hydride ion promoted solubilization process and the successful demonstration of the pressure filtration step in Task 2 form the basis for integration of the two process steps in Task 3. The transfer of first-stage product from the one-liter stirred autoclave to a receiver vessel, as executed in Task 2, provides the necessary experience for insertion of a filter between the reactor and the receiver vessel. A pre-filtration flash of the light distillate will be included in the design and construction of the coupled first-stage reactor and filter apparatus.

The high, single-pass resid conversions obtained in the second-stage catalytic upgrading studies warrant the design and testing of a larger scale catalytic reactor in Task 3. The scale of the reactor will be such as to accommodate the entire filtrate from a single experiment.

The economic and engineering evaluation will be continued and expanded as the program proceeds. Conceptual commercial plant designs will be finalized in Tasks 3 and 4. Data generated in bench-unit tests will be compared in Tasks 3 and 4 to a base case using a similar coal. In order to eliminate differences in product slates between cases, each plant will include an upgrading section to convert the product to a finished transportation fuel (gasoline). The

capital and operating costs of the conceptual plants will be evaluated, thereby generatinga quantitative assessment of the merit of the proposed novel concept.

# INTRODUCTION

The development of coal liquefaction over the past decade has been marked by the steady improvement in a rather narrowly defined range of process concepts characterized by a thermal or catalytic coal dissolution at temperatures above the conventional pyrolysis range, followed by a catalytic conversion of the dissolved coal (or coal-derived resid) to distillate products. Significant advances have been made in yields, selectivities, and product qualities, all of which provide corresponding cost advantages. However, future improvements in the "conventional liquefaction" approach will have a diminishing effect on further cost reduction. Higher risk cutting-edge technologies may have the potential for substantial cost reductions. One such novel coal liquefaction technology is being investigated in this program.

CONSOL Inc., the University of Kentucky Center for Applied Energy Research, and LDP Associates are conducting a three-year research program under DOE Contract DE-AC22-95PC95050 to explore the technical and economic feasibility of the novel concept of hydride-ion transfer liquefaction. The work is organized into five Tasks. This report describes the work performed under Task 2, "Evaluation of Process Steps". The process steps are: 1) a first-stage low-temperature coal solubilization, 2) filtration of the first-stage products, and 3) a second-stage catalytic upgrading of the filtrates. The program was designed to first evaluate each process step and then to evaluate the integration of the steps into an overall process. Concurrent with the experimental evaluation of these three steps, an engineering and economic evaluation of each step was conducted to provide guidance at key decision points and to provide criteria for deciding on experimental alternatives.

## SOLUBILIZATION AND PRODUCT CHARACTERIZATION

The objective of the first-stage solubilization step is to explore a new, low-severity approach to direct coal liquefaction in which the primary coal dissolution step is effected by chemical rather than thermal cleavage of bonds in the coal. This novel coal liquefaction method is based on the discovery made by CONSOL R&D[1] that certain reagents are capable of hydrolyzing to form hydride transfer agents that are very active for coal dissolution at temperatures in the range of 350-400 °C. These temperatures are significantly lower than those typically used in coal liquefaction. Reaction at these low temperatures results in high conversion of the coal to a solubilized form, with little hydrocarbon gas make, and avoids the thermally induced retrograde reactions which are unavoidable in conventional thermal processes. In addition, for low-rank

coals, a substantial portion of the oxygen in the coal is removed as CO and $CO_2$ during the dissolution. It is believed that the higher selectivity to liquid products and rejection of oxygen as the carbon oxides should result in improved hydrogen utilization.

Although a detailed reaction mechanism has not been determined, the overall chemistry of the reaction is believed to involve hydrolysis reactions promoted by the hydride reagent. Hydrogen is supplied to the depolymerizing coal from either water introduced into the reaction as the inherent moisture in the coal or by addition of water to the reaction system. Therefore, there is no need for hydrogen (or other reducing gas) to be introduced into the dissolution reactor. The species produced by hydrolysis of the hydride reagent then effects a hydride ion donation to the coal. The two reactions take place sequentially in the first-stage reactor. This necessitates operating in a temperature range where the rates of hydrolysis and hydride transfer are approximately the same. The range (350-400°C) tested in Task 2 of this program is believed to be such a region.

FILTRATION

The primary requirement of the solids separation stage in any coal liquefaction process is to ensure that solids are not present in the premium products. Solids, ash, and insoluble organic matter (IOM) must be separated at some stage in all direct liquefaction processes. For obvious economic reasons they should be removed at as high a concentration as possible, i.e., they should not be diluted with primary (of higher value) products any more than absolutely necessary.

Removal early in the processing scheme is often advantageous as this reduces the overall size and cost of subsequent processing equipment. Coal cleaning to remove some of the ash from the coal feed is one such example. For the process to be viable, however, the cost of the processing must be more than compensated for by the economic benefits. Reducing the solids content of the process stream has the added advantage of significantly reducing erosion of reactor components, thereby requiring less severe construction material specifications and consequently reducing costs. Filtration offers a good potential for cost-effective solids removal. It is the preferred method of solids separation, provided reasonable flow rates can be achieved.

The size distribution of the solids removed may be very wide, ranging from the size of the coal feed to micrometer size particles of inherent ash and fragmented partially dissolved coal

macerals. The use of mild extraction conditions with some coals may result in the formation of particles that are still soft and plastic. Both the wide size distribution with a predominance of the fine particles and the plasticity of some of them can result in the formation of filter cakes whose permeability is so low that the filtration rates are unacceptable. In extreme cases, blinding of the filter can occur when flow through the filter is no longer possible.

It is not only the solids comprising the filter cake that affect flow rates through the filter unit, but also the viscosity of the fluid phase in the coal liquefaction product. Its impact will depend upon a number of factors including solvent type, solvent-to-coal ratio, and the processing conditions. Mild liquefaction conditions produce extract of much higher molecular weight (MW) and viscosity than are produced at more severe conditions. For example, extraction with a non-hydrogen donor solvent may not significantly affect the coal structure, so that on removal of the solvent an extract is produced that is essentially the same as the original coal, but without ash and some macerals. Such a pure extract would be expected to soften at 350-450 °C.

Cake resistivity (or permeability) and fluid viscosity are important parameters in determining flow rates. However, viscosity can be controlled to a certain extent by altering the operating temperature and the solvent to coal ratio. High cake resistivities may be more difficult to contend with. Modification of extraction conditions or incorporation of filter aids may be necessary to deal with very high cake resistivities, if encountered.

Filtration economics are based on the cost of filtration per unit weight of coal processed or of product produced. Thus, the rates achieved in the laboratory need to be related to an industrial filtration cycle in which the downtime associated with the filling and emptying the filter and the additional processes of washing and drying the filter cake must be considered.

Filtration rate slows as the cake thickness builds up. This requires calculations to be made of the optimum cake thickness that gives the fastest overall rate (i.e., the smallest filter for a specific coal throughput). The maximum overall rate is achieved when filtration time and down time are of equal length.[2] Even the simplest cycle on a commercial scale will have a downtime of at least 15 min and more likely 25-50 min. Thus, the average rate of filtration over 15-50 min is relevant to commercial operation, and the overall rate will be only half the observed filtration rate.

Order of magnitude calculations (Appendix 3) show that if a rate of filtration in the laboratory is 200 kg/h/m$^2$ over a period equal to the down time (e.g., 30 min) then the overall cost of filtration is about 40-50¢/bbl Crude Oil Equivalent (COE). This would appear to be an acceptable cost. Higher rates of 1000 kg/h/m$^2$ would give big savings by bringing the cost down towards 10¢/bbl. Conversely, lower filtration rates of under 100 kg/h/m$^2$ would result in costs of over $1/bbl.

The allowable cost of filtration is directly related to alternative solid liquid separation methods. Comparisons previously were made among critical solvent deashing (ROSE-SR), vacuum distillation and filtration in ITSL[3] in which it was concluded that filtration has an advantage of 20¢/bbl. This is because the discharged reject stream contains far less valuable liquid product (90% solids in the vacuum dried cake compared with 50% solids in the vacuum distilled bottoms) and enables a reduction in the first stage reactor throughput for the same oil production rate. Another way of expressing this difference is to consider the total amount of material rejected with the ash in each case. Typically, for a coal containing 10% ash, the IOM will similarly be 10% following liquefaction (90% conversion). However, the discharged vacuum bottoms will contain an equal amount of liquids as solids, resulting in an effective "coal conversion" in the first stage of only 70%. For filtration, the dried cake will contain only 10% non-IOM and ash material, i.e., conversion will be 88%. ROSE-SR units would give an intermediate value. This extra conversion realized in practical processes is worth a significant amount (for example the amount of effort expended in order to improve first stage conversion by a few percent by coal cleaning, is generally accepted as cost effective).

Thus, based upon the higher process yields, filtration can be economically viable even if the costs are more than other separation methods. It is unlikely that these benefits are worth several dollars per barrel; therefore, in general terms, laboratory rates of 10 kg/h/m$^2$ could be deemed almost acceptable, 100 kg/h/m$^2$ definitely acceptable and 1000kg/h/m$^2$ extremely attractive.

An expanded discussion of filtration theory and practice can be found in Appendix 4.

## CATALYTIC UPGRADING

In the second-stage reactor, the solids-free first-stage product will be converted to light distillate by catalytic hydroprocessing. The nature of the material produced by hydride ion promoted coal liquefaction was not well understood. Consequently, its reactivity as a feedstock for upgrading, and the critical operating parameters were sought in Task 2.

Upgrading the solids-free first-stage liquefaction product by catalytic hydrotreating to distillate products requires hydrogen addition, molecular weight reduction, and heteroatom removal. These reactions can be conducted in the presence of either dispersed or supported catalysts. A solids-free feed to the second stage offers some novel prospects for the use of dispersed catalysts; thus, greater emphasis was placed upon investigations with this form of catalyst.

A low purge rate of unconverted bottoms from an upgrading reactor would allow for the use of high-activity dispersed catalyst in high concentration. Molybdenum was shown in previous work to be a preferred catalyst metal for upgrading coal-derived products. It can be conveniently added to the reactor in the form of an oil-soluble precursor. Two candidate precursors were identified in other studies: the catalyst precursor used in the Wilsonville pilot plant operation, Molyvan L, and molybdenum naphthenate, which is reported to be an effective catalyst precursor for a petroleum resid upgrading process under development by Exxon.[4,5]

To produce an active (sulfided) form of the dispersed catalyst representative of the behavior of the catalyst in a larger scale continuous plant, thermal pretreatment may be necessary. To determine if there is a benefit in thermal pretreatment, a study was undertaken in Task 2 using a number of treatment conditions.

In order to obtain information about the product distribution and selectivity to distillates and the kinetics of resid conversion, a parametric study using a single batch of filtered liquefied low rank coal was made. Parameters investigated were molybdenum concentration, reaction temperature and reaction time. These experiments were designed to assess the product distribution, hydrocarbon gas yield, the conversion per pass of residual product, the hydrogen consumption, the final form of the catalyst, and the extent of formation of any carbonaceous solids.

## ENGINEERING AND ECONOMIC EVALUATION

Previous scouting studies indicated that the novel concept being investigated in this program is chemically feasible. However, to move this concept into the process-development stage a demonstration of both technical and economic feasibility are required. Therefore, concurrent with the physical and chemical reaction research an engineering and economic evaluation is being carried out. This evaluation will be sufficient to define the incentives (or lack thereof) for actual process development.

The synthesis and regeneration of the hydride ion reagent will be a key factor in the economic feasibility of the process. In Task 2, the best commercial options for synthesis and regeneration of the hydride ion reagent were investigated.

The project was begun with a preliminary conceptual process design, which served as the framework within which testing of the reaction steps was initiated in Task 2. Refinement of this design was based on the results obtained in Task 2. The design that was produced in Task 2 allows for testing the reaction steps in an integrated fashion in Task 3. The conceptual design formulated in Task 2 may not be the final design of the process; further refinement will reflect the information gathered in Tasks 3 and 4.

# EXPERIMENTAL

## SOLUBILIZATION AND PRODUCT CHARACTERIZATION

### MICROAUTOCLAVE TESTS

#### Equipment

The microautoclave tests are made in 45 mL stainless steel microautoclaves (Figure 1). The microautoclaves are shaken vertically in a fluidized bath of alumina sand at 1000, 1/2" strokes per minute. A 1/4" stainless steel ball is inserted in the microautoclave to aid in mixing.

#### Coals

Five coals have been tested in the microautoclave test program. They are: Freedom Mine North Dakota lignite (high-ash, high-sodium sample); Freedom Mine North Dakota lignite (low-ash, low-sodium sample); Glenharold Mine North Dakota lignite; Black Thunder Mine Wyoming subbituminous coal; Ohio 11 Mine, western Kentucky bituminous coal. Analyses of these coals are given in Table 1.

#### Solvents

Six solvents were used in the microautoclave tests: 1) the full-boiling range material, 2) a (488 °C$^-$) distillation fraction of the recycle solvent (V 1074) from the Wilsonville Two-Stage Direct Coal Liquefaction Pilot Plant, Run 262 Period E, 3) a Lummus pasting solvent distillate (Run 3LCF7), 4) an anthracene oil obtained from Reilly Industries, 5) an anthracene oil from Kawasaki Steel Corporation, and 6) tetralin. Analyses of the five coal-derived solvents are given in Tables 2 and 3.

#### Hydride Ion Reagents

Three hydride ion sources were tested in the program. They are designate hydride ion (H$^-$) reagent "A", "B", and "C". Descriptions of the three reagents are given in Confidential Appendix I. In addition, tests were made with CO and CO/methanol.

#### Test Sequence

The sequence for typical coal liquefaction runs was as follows. Charges of coal, solvent, hydride ion reagent, and water (if used) were weighed into the tared microautoclave body. The total charge used in the experiments ranged from 9 g to 35.3 g. The atmosphere in the head space in most runs was ambient air. When CO was used, after all solid and liquid reagents were

changed, the reactor was flushed with CO; a charge of CO then was introduced per run plans. Charge pressures were between 150 and 1490 psi (cold). After sealing, the vessel was connected to the shaker apparatus and shaking was started. While shaking, the microautoclave was lowered into a preheated sand bath. Reaction temperatures were achieved in two min (four min for slow heat-up rate tests). Reaction temperatures were primarily 350, 375, and 400°C. In select experiments, heating rate was investigated. To accomplish this, the bath temperature was set at 200 °C and allowed to rise to final reaction temperature after the microautoclave was immersed in the sand bath. Heating rates were either 1 °C or 2.5 °C/min. At the end of the prescribed residence time the microautoclave was withdrawn from the sand bath and immersed in a tank of ambient-temperature water while still shaking. The contents were quenched to ca. 100 °C in less than 90 sec. Reported reaction times include the time from immersion of the microautoclave in the sand bath until immersion in the water bath.

A post-run weight was obtained to check for leaks. The microautoclave was attached to a pressure gauge at the fitting above the fill valve (Figure 1). It then was submerged in a dry ice/acetone bath until the internal thermocouple read -70 °C. The valve was opened and a gas pressure reading was obtained. The microautoclave was removed from the dry ice/acetone bath and allowed to slowly warm to room temperature, pressure was continually monitored as the vessel warmed. When the internal thermocouple registered room temperature (20-22 °C), a final pressure reading was recorded. A weighed $Mg(ClO_4)_2$ water trap was attached to the outlet of the microautoclave and the gas was vented into a one-liter evacuated chamber from which it was sampled for GC analysis. Gas chromatography was performed using a four-column Carle Model III analytical gas chromatograph. A standard gas mixture (Table 4) was used for GC calibration. The remaining gas was vented. The $Mg(ClO_4)_2$ water trap was weighed. The microautoclave and contents were reweighed. Gas make was determined by the difference in the weight before the tests and after venting.

Sodium Addition

Sodium was added in small amounts to the low-ash sample of Freedom Mine North Dakota lignite. In some tests, a sodium salt of a hydride ion reagent, Hydride Ion Reagent “C” (HI”C”) was introduced as a water solution at a level equivalent to increasing the sodium (as $Na_2O$ on ash) to 11 wt %. The coal-hydride ion reagent mixture was allowed to air dry to reduce the moisture level to that of the starting coal. Three times the amount if HI “C” was introduced as a water solution; the coal-HI “C” mixture was left in a tumbler for 72 hours to ensure good mixing.

The residual added water was about 0.4 g. HI "A" was used as the hydride ion source in these tests. HI "C" was substituted for HI "A" in a third set of tests. It was added to the reactor as a dry crystal and as a water slurry in an equimolar amount to HI "A" used previously.

Non-Gaseous Product Work-Up

Three procedures were followed, depending on the eventual use of the non-gaseous products.

Coal conversion determination

The microautoclave head was removed. The entire reactor contents were removed to a pressure filter apparatus by washing with freshly distilled tetrahydrofuran (THF). A tared Whatman 42 ashless filter paper was used to back a tared glass fiber filter (Whatman 934-AH) in the pressure filter apparatus. Filtration was carried out under 5-15 psi $N_2$. Filtration was continued until the filtrate was nearly colorless. The filter cake was dried at 100 °C for minimally 4 hours. Coal conversion was determined on an $SO_3$-free-ash-free basis as follows:

$$coal\ conversion = 100 - \frac{filter\ cake - SO_3\ free\ coal\ ash}{MAF\ Coal}\ x\ 100$$

Preparation for Filtration Tests

The microautoclave head was removed. A distillation head was attached. The microautoclave body was encased in a custom-designed heating mantle. The microautoclave was heated to a temperature of 121 °C to remove low-boiling reaction products and water. The microautoclave was allowed to cool and the contents were removed to shipping containers.

Material Balance and Product Analyses (Figure 2)

The microautoclave head was removed. A distillation head was attached. The microautoclave body was encased in a custom-designed heating mantle. The microautoclave was heated to a temperature of 121 °C to remove low-boiling reaction products and water. The 121 °C$^-$ fraction was analyzed by $^1$H-NMR spectrometry. The microautoclave was allowed to cool and the contents were removed to a pressure filter apparatus by washing with freshly distilled tetrahydrofuran (THF). A tared Whatman 42 ashless filter paper was used to back a tared glass fiber filter in the pressure filter apparatus. Filtration was carried out under 5-15 psi $N_2$. Filtration was continued until the filtrate was near colorless. The filter cake was dried at 100 °C for minimally

4 hours. Coal conversion was determined as described above. The filter cake was analyzed for weight percent C, H, N, $S_{tot}$, and ash. The THF-soluble fraction was partially stripped of THF on a rotary evaporator. The 121 °$C^+$ material was placed in a (50 mL) distillation flask and distilled under 5 torr to 292 °C (488 °C atmospheric equivalent) to remove process solvent. The 488 °$C^-$ fraction and the 488 °$C^+$ solubilized coal product were analyzed for weight percent C, H, N, $S_{tot}$, and O (by diff).

## ONE-LITER AUTOCLAVE TESTS

### Equipment (Figures 3 through 7)

The reaction vessel (Unit A-1) is an Autoclave Engineers, 1 liter, MagneDrive stirred autoclave; 7.62 cm ID x 22.86 cm IL, 316 SS, maximum working pressure 39.9 MPa (5800 psi) at 343°C (650 °F) equipped with thermocouple well, pressure tap, rupture disc (rupture pressure: 378 MPa (5500 psi) at 72 °F) and cooling coil. The high-pressure receiver (Unit R-1) is a Pressure Product Industries, 3.78 L (1 gal), 316 SS, pressure vessel, 12.7 cm (5" ) ID x 30.5 cm (12" IL), maximum working pressure 34.5 MPa (5000 psi) at 93°C (200 °F); equipped with thermocouple well, pressure tap, and rupture disc (rupture pressure 30.9 MPa at 72 °F). This vessel is contained and conveyed mounted on a hydraulic-lift hand cart which provides for pivoting the vessel on 1" pillow block bearings fastened to hand cart forks. The high-pressure separator is a Pressure Product Industries, 3.78 L (1 gal), 316 SS, pressure vessel, 12.7 cm ID x 30.5 cm IL, maximum working pressure 34.5 MPa at 93 °C (200 °F); equipped with thermocouple well, pressure tap, and rupture disc (rupture pressure 30.9 MPa at 72°F).

### Test Sequence

The one-liter autoclave unit was designed to be operated in one of three configurations under Task 2. In Configuration 1 (Figure 3) reactants are introduced, the autoclave is sealed and the run executed. At the conclusion of the run, the products are recovered from the autoclave unit. In Configuration 2 (Figure 4), a 1 gal receiver vessel (R-1) is attached to the 1-L autoclave and products are recovered by transfer to the receiver. The autoclave does not contain a cooling coil in this configuration. Configuration 3 (Figure 5) includes vessel R-1 and a 1-gal separator vessel (S-1) in which gases and condensable vapors will be separated from liquid products Configurations 1 and 2 have been tested under Task 2.

Run termination and collection of liquids and permanent gases can be accomplished by one of four methods. The gas collection system is shown in Figure 6. In Method 1 (Figure 3) gases are

quantitatively collected from the cooled sealed autoclave (A-1) after the conclusion of the run by venting to a gas collection system; vapors are condensed in dry-ice cooled condensers, permanent gases are collected in a gas-collection vessel. After the gas is sampled, remaining gas is vented. Liquids can be drained from A-1 or removed by removing the reactor head. In Method 2 (Figure 4) at the conclusion of the run, products of reaction are transferred from the reactor to the receiver vessel (R-1); gases are collected from the cooled reactor system (autoclave plus receiver vessel) as in Method 1. After the gas is sampled, remaining gas is vented. Liquids are obtained by removing the receiver vessel head. In Method 3 (Figure 7), at the conclusion of the run, products of reaction will be transferred from the reactor to the receiver vessel (R-1) which will be maintained above the calculated temperature at which the steam will condense; gases and condensable vapors (including steam) will be transferred from the receiver vessel to the gas collection system. The vapors will be condensed in dry-ice cooled condensers, permanent gases will be collected in gas collection vessels, after sampling the remaining gas will be vented. In Method 4 (Figure 5), gases and vapors will be transferred directly from the hot reactor to a disengaging chamber (separator, S-1); vapors will be condensed in dry-ice cooled condensers, permanent gases will be collected in gas collection vessels and the remaining gas vented. Liquids collected in S-1 will be transferred to receiver vessel R-1. Liquids remaining in the reactor (A-1) will be transferred directly to the receiver vessel. Liquids will be obtained by removing the receiver vessel head. Methods 1 and 2 were executed under Task 2.

## FILTRATION

### Micro-Filtration Rig

The filter body (Figure 8) consists of a length of thick wall stainless steel tubing 19 mm o.d x 14.5 mm i.d., 154 mm long with reducing compression fittings (Swagelok; 19 mm to 6.3 mm) at each end. The filter medium was housed in one of the fittings and consists of a type GFA glass fiber paper sandwiched between two perforated stainless steel discs, 0.4mm thick with 0.5 mm dia. holes, open area ~20% (provided by Ferguson Perforating and Wire Company). Alternatively, a single piece of Conidur (Hein Lehman of Dusseldorf) 0.35 mm thick stainless steel sheet with perforations of nominally 100 µm x 500 µm and an open area of about 5% is used. In the other end, a baffle made from 0.35 mm thick stainless steel sheet was initially installed to prevent loss of sample from the filter during heat-up, when the filter was in the horizontal position.

The filter was pressurized and vented via a 6.3 mm o.d. tubing connection. Pressure was measured using a transducer with digital output. A ball valve fitted with an extension handle was connected to the outlet from the filter housing via a short piece of 6.3 mm o.d. stainless steel tubing. The filter body, both end fittings, and the outlet valve were fitted inside a split cylindrical furnace (Applied Test Systems Inc. series 3210, 800 watt) which was mounted on a framework that enabled it to be placed in either horizontal (for heating) or vertical position (for filtration). The temperature of the furnace was controlled by an internal thermocouple and a temperature controller (Omega 4002 KC).

The temperature of the filter body was measured initially by a thin, unsheathed thermocouple which was placed on the filter body near the lower fitting; this thermocouple was held in place by the clamping action of the split furnace. In later experiments, when the internal baffle was not used, a sheathed thermocouple was installed within the filter via a tee in the inlet pressure line. Filtrate was collected in glass sample bottles standing on a top-loading balance.

Procedure

The samples were received in glass bottles. These were weighed and then heated in air to 66 °C (150 °F) for one hour, and then to 135 °C (275 °F) for another hour and reweighed after each heating period. The objective of this procedure was to remove any remaining light oil and water while the sample was retained in a system that could cope with any foaming that occurred (the heating rate and temperature were much lower and the dead space and cross-sectional area of the sample container were much larger than in the micro filter).

The filter components (e.g., barrel, filter, fittings and outlet valve) were initially weighed before the filter body was assembled. The 6-7 g sample was loaded into the filter unit. The sample was usually of a thick paste consistency and was removed from its jar using a spatula, placed on a semi-cylindrical carrier, then pushed into the filter using a third implement. This last item was sometimes heated to assist transfer. The filter was reweighed to determined the weight of the sample transferred.

After assembling the components, the filter was placed into the preheated furnace. In some tests the heating was performed with the filter in a horizontal position, at other times in the vertical position. With a control temperature of 350 °C, the filter reached the normal operating tempera-

ture range of 250-300 °C in about 30 min. During this period, the filter was vented to the atmosphere via a condensing pot.

Filtration commenced by pressurizing the filter with nitrogen, opening the outlet valve, and starting a stopwatch. The increasing weight of the filtrate was recorded as a function of time. With particularly viscous feedstocks it was necessary to keep the outlet pipe warm with the aid of a hot air blower. After filtration was completed (flow of filtrate stopped and gas break through observed) the filter was depressurized, the furnace switched off, and the filter assembly was removed from the furnace. When cool, the filter was disassembled and the component parts weighed. Where possible, the filter cake thickness was measured and its volume estimated.

200 mL Filtration Rig

The configuration of the 200 mL filtration rig is similar to that of the micro-filtration rig described above. The length of the 35 mm i.d. stainless steel filter body is 225 mm with a capacity of 200 mL, and the flanged lower end houses a 47 mm diameter filter. The same type of filter elements were used as in the micro filtration tests; i.e., either GFA filter paper sandwiched between perforated metal supports, or a Conidur element. A silicon rubber O-ring served both as main gasket and to seal the filter screen into the housing. The flanges were secured with three bolts and wing nuts. The filtrate outlet was through a 4 mm bore ball valve containing a Teflon seal. The top of the unit was closed with a flanged lid containing a pressure port and a relief valve set to 0.7 MPa. This was held in place with a quick release clamp and sealed with a Teflon ring.

The filter was heated in a 75 mm i.d. x 127 mm o.d., 152 mm cylindrical furnace (Omegalux, CFRC 36/115, 700 watt). A variable transformer, manually adjusted, was used to control the temperature of the unit by monitoring the internal filter temperature measured with a sheathed thermocouple entering the vessel via the pressure port.

Procedure

The operating procedure for this filter was similar to that of the micro-filtration rig with the exception that the larger sample size required a different loading technique. The sample was preheated either in glass flasks within a mantle or in an insulated stainless steel beaker on a hot plate. In both cases, the feed material was mixed by agitating with a magnetic stirrer bar immersed in the sample. The sample was transferred manually to the pre-heated filter, the

upper flange quickly closed, the filter pressurized, and the outlet valve opened. In one test, a step-wise increase in nitrogen pressure was made during filtration in order to assess the compressibility of the cake. In the same test, filtration was temporarily stopped just prior to its natural completion and 10 g of distillate (from a similar feedstock) was added to the filter chamber; the filtration pressure was then reinstated and further filtrate (washings) collected.

One set of samples was treated differently (i.e., the Run 8-LA set). The first materials received (Runs 8a-LA and 8b-LA products) were intended to be mixed together for homogenization, then split into several subsamples. The combined sample was designated 8ab-LA. However, this homogenization was not feasible. Even when the sample was heated to over 200°C, solids were observed that settled very rapidly. This is indicative of the presence of coal extract that had precipitated from solution following cooling from the first-stage reaction temperature. An initial separation was made by decanting the liquid (lights) from the solids (heavies), then subsampling these fractions to make representative reconstituted samples just prior to filtration. A third sample, Run 8c-LA product, was similarly treated. The decanting temperature was 65 °C, compared to 250 °C for Run 8ab-LA. Heavy coal tar distillate was added as diluent to some of the samples prior to filtration.

## Product Work-Up

### Filter Cakes

The amount of material insoluble in tetrahydrofuran (THF) was determined for each filter cake. The filter cake is crushed and either a 1 g representative sample or the whole sample, if less than 1 g, is mixed with 20 mL of THF and continuously stirred for about one hour at a temperature of ~30 °C. The slurry is vacuum-filtered through a pre-weighed glass fiber paper, washed with more THF, and dried in an air oven at 70 °C. In some cases, THF insolubles from the filter cake or the filter cake itself were analyzed for ash content (and occasionally for sulfur content).

### Filtrates

Selected filtrates were analyzed for THF solubility and ash content as above. Where feasible, the viscosity of coal solutions was measured over a temperature range of typically 100-300 °C, using a Brookfield LVT viscometer with Thermosel unit. Measurement of viscosity at values of less than about 10 mPa•s are liable to error with this instrument. However, at high temperatures many coal solutions have viscosities lower than this value; in those cases, the determination was

made by extrapolation using known relationships between viscosity and temperature (Figure 9). These values can be used with confidence only over small temperature ranges. Measurements for inhomogeneous samples where filtrates had separated into two phases, a light-solvent-rich fraction and a heavy-extract-rich fraction, could be made only at a temperature where all the extract was solubilized and before there was evaporation of light components. Only a narrow temperature range is then available for viscosity measurements.

Where there was insufficient sample (<10g) or the sample was too viscous for the measurement of viscosity, the softening point was determined by using a Mettler FP5 instrument or by estimation from visual observation. This technique, in which a thermocouple was used to agitate the sample on a heated surface, has proven remarkably reliable. The softening point of a fluid is the temperature at which its viscosity is approximately $10^6$ mPa·s. The viscosity at other temperatures can be estimated, but a degree of caution is required in using these estimated values.

The boiling point distribution of selected samples was determined by simulated distillation (see below).

In order to prepare feedstock for second-stage catalytic upgrading tests, selected samples of filtrate were vacuum distilled to concentrate the coal extract content. For second-stage micro-autoclave tests, several filtrates had to be combined to provide adequate quantities.

## CATALYTIC UPGRADING

### General

### Equipment

The catalytic upgrading experiments were conducted in batch reactions using microautoclaves (Figure 10). The nominal 50 mL microautoclaves used in this study were made of 1.0 in diameter x 0.120 in wall, type 316 stainless steel tubing with Swagelok socket weld-to-tube ends, capped with two 1 in plugs. The overall length of each reactor body was 6 in with the end plugs removed. The microautoclaves were mounted with the cylinder axis horizontal, and connected by a weld at the middle of the tube body with a vertical 1/4 in stainless steel tube to allow gas pressurizing and venting. The vertical tube is attached at its upper end to a Swagelok tee fitting which is connected to a coil of 1/8 in diameter type 316 stainless steel tubing (0.035 in wall). A valve at the end of the coil seals the reactor and serves as the mechanical connection

for a pressure transducer. The real-time measurements of both the reaction temperature and pressure are performed using an 8-channel Omega 12-bit card in a Gateway 486-33 computer. The operating limits of the microautoclaves are 18.7 MPa (2700 psig) and 440°C. The calibration of the pressure transducer was checked against a 2.86 MPa(400 psig) test gauge and a hydrotest gauge at 17.3 MPa (2500 psig). The reactor size (50 mL) provides ample hydrogen for the hydrotreating reaction.

Methods

In a typical experiment, 3 g of feedstock and the appropriate amount of catalyst precursor are added to the reactor. The reactor is purged with hydrogen, pressurized to 10.1 MPa (1450 psig) total pressure (2% hydrogen sulfide, balance hydrogen), sealed, and leak tested. The reactor then is attached to the agitation (dashing) apparatus. The pressure transducer is connected to the reactor via an 1/8 in tubing coil, and the initial pressure at room temperature is recorded. The reactor is heated by immersing it into a hot, fluidized sandbath. For some experiments, a pretreating period is implemented in which the reactor is heated in the sandbath at a lower temperature for a specified period of time before it is heated to the higher reaction temperature. The lower temperature of the pretreatment period is achieved by modulating the reactor at the surface of the sandbath. During pretreatment and reaction, the reactor is continuously agitated by vertical displacement at a rate of 350 cycles per minute, which is verified by a strobe light tachometer. At the end of the reaction period, the reactor is immersed into an ice-water bath for rapid cooling to ~25°C and the final pressure of the reactor is recorded. The reactor temperature and pressure are continuously monitored and recorded by the computerized data acquisition system.

Following quenching, the reactor is vented into a 10 L gas piston collection cylinder at atmospheric pressure. This serves to accurately measure the gas volume and to collect a representative gas sample for subsequent analysis (see next section). The liquids then are scraped from the autoclave with the aid of THF (without stabilizer), and transferred to a 100 mL two-neck, round-bottom distillation flask. Vacuum distillation, as described in the following section, is performed on the mixture of product liquids and THF from the washing procedure.

## Product Analyses

### Gas Analysis

The gas mixture from the reactor is collected in the 10 L acrylic syringe. It is pumped with a metal bellows pump through the sampling valves of a Carle Series AGC 400 Refinery Gas Chromatograph (Application 397-B) at a rate of 20 mL/min. The multi-column, dual-detector (FID, TCD) GC separates $H_2$, $CO_2$, CO, $H_2S$, $N_2$, $O_2$ and hydrocarbons from $C_1$-$C_5$. By backflushing the column once $C_5$ materials pass the switching valve, a lumped peak of vapor-phase $C_6$+ hydrocarbons also is obtained. Analysis time is 20 min. Calibration is performed daily with a primary standard, and analyses are performed in triplicate.

### Vacuum Distillation

Vacuum distillations are performed using a modified ASTM D-1160 procedure on the non-gaseous products.[a] The distillation apparatus consists of a distillation flask equipped with a thermowell, a distillation head equipped with a thermometer, and an adapter with a sidearm connecting the distillation head to the receiver flask. A 2.1-cm long Teflon-coated magnetic stir bar is placed into the distillation flask. A known weight of vacuum grease (~0.2 g) is applied to the ground glass joints. A Thermix magnetic stirrer is used to drive the magnetic stir bar. A GlasCol heating mantle and two 2 ft long x ½ in wide heating tapes are used to apply heat to the distillation flask and distillation head. The apparatus is liberally wrapped in Fiberglass insulation.

The essentially solids-free sample is placed into the distillation set-up. While stirring, the flask is slowly heated to ~120 °C at ~0.5 atm to remove light material including any remaining THF and entrapped air. During this period, care must be taken to prevent bumping. At ~120 °C the vacuum is increased slowly to 1 torr while stirring. The temperature is increased from near ambient to 331 °C over a period of about one hour, depending on the amount of residual THF present. Once the cut point has been reached, heating of the apparatus is discontinued. The flask is allowed to cool while caution is taken to prevent liquids collected in the ice trap from backing into the distillation apparatus. Once the apparatus has returned to ambient temperature, the weight of each individual glassware section is obtained. The contents then are calculated, assuming that grease contained on the joint connecting the distillation head and the adapter

[a] Standard Test Method for Distillation of Petroleum Products at Reduced Pressures, Method No. D-1160-87, 1990. In: Annual Book of ASTM Standards, Am. Soc. Testing Materials, Phila. Vol 05.01, page 419.

remains on the distillation head. The holdup in the distillation head is assumed to remain entirely with the residual fraction. The atmospheric equivalent temperature (AET) is calculated from the actual cut point obtained in the microdistillation apparatus by the following equation:

$$AET, °C = \{(748.1 * A)/[1/VT+(0.3861*A)-0.00051606]\}-273$$

where:

A = ([5.9991972-(0.9774472*log P)]/[2663.129-(95.76*log P)])

VT = vapor temperature in Kelvin

P = pressure of system in mm of Hg (Torr) observed when the vapor temperature is read

The AET for an observed distillation temperature of 331 °C at 1 Torr is 566 °C (1050 °F), which simulates the separation obtained in the vacuum tower at the Wilsonville Advanced Coal Liquefaction Facility. Material balances are based upon a forced catalyst balance with any loss and error being assigned to the distillate product. Resid conversion is calculated as follows:

The vacuum distillation serves not only to provide a boiling-point measure of conversion for residuum feedstocks, but also acts as a preparation step for subsequent analysis. The distillate and bottoms fractions from the distillation procedure are often available in sufficient quantities for both ultimate analyses and simulated distillation. Ultimate analyses are performed according to ASTM specifications for selected experiments.

High-Temperature Simulated Distillation

In order to more fully characterize the products of the upgrading step and to confirm the accuracy of the distillation cut point, a high-temperature simulated distillation method was developed. The high-boiling nature of the coal-derived liquids studied in this work required a simulated distillation method capable of handling materials boiling above 566 °C at atmospheric pressure. The simulated distillation apparatus and method that were chosen were developed by AC Analytical Controls, Inc (AC). The method is designed to analyze hydrocarbons up to a boiling point of 750 °C. The apparatus consists of a Hewlett-Packard model 6890 gas chromatograph. It is operated under the conditions listed in Table 5. This method developed by AC Analytical Controls (HT 750) is a higher temperature extension of the Extended D2887 simulated distillation. Neither the Extended D2887 nor the HT 750 methods are official ASTM methods, although the procedures are similar to ASTM D2887.

In the HT 750 method, three solutions are injected as part of the calibration procedure: a $CS_2$ blank, boiling point calibrant, and reference oil. An injection of pure $CS_2$ is made and data are collected under the same analytical conditions as the sample analysis. These data are subtracted from the sample and reference oil data, correcting for the $CS_2$, FID/system noise and column bleed. The software automatically compares the signal area with previous blank areas to determine if shifts have occurred. In addition, the blank is checked for extraneous peaks, which indicate errors.

Polywax 655, combined with light n-alkanes $C_5$ through $C_{28}$, is injected to establish the boiling point calibration slope. The software indexes on peaks within this material and performs linear regression to calculate high boiling data for peaks that might not be detected. This might occur in the range of $C_{90}$-$C_{120}$. The software compares previous boiling point slope data with the current data to check for errors and gradual shifts indicative of stationary phase deterioration in the column. The symmetry of each peak is evaluated and the skew is reported.

The final step in the calibration procedure is the injection of a reference oil sample. This material is used to calibrate the system as an external sample for all sample recovery calculations. In addition, the software is programmed with the physical weight distillation data (D2892) of this sample. The software calculates and reports the target versus actual boiling point data and reports the statistical error of the difference.

The procedure described above was designed for petroleum-derived materials which are typically aliphatic in nature. Coal-derived materials are highly aromatic in nature. On a non-polar column, aromatic compounds elute faster than aliphatic compounds of similar boiling point. To quantify this behavior, the retention times of a mixture of condensed-ring aromatic compounds were compared to those of the paraffinic calibrant (Figure 11). For the higher-boiling materials, there are differences of approximately 56 °C (100 °F) between aliphatic and aromatic compounds of similar retention time. A way to account for the difference in behavior would be to use an aromatic mixture as the daily calibrant. However, it would be difficult to produce a calibration mixture of aromatics that extends to a boiling point of 750 °C as does the Polywax 655. The identification and purification of aromatics that boil higher than coronene (977°F) is not practical. Moreover, coronene occurs as a broad and irregular peak (Figure 12) and is not ideal for an automated calibration procedure. Consequently, a method of adjusting the boiling point vs. retention time relationship for aromatics was developed which is based on both the

aromatic and paraffinic calibration mixtures. By extrapolating the aromatic calibration to 750 °C, it is possible to create a mathematical relationship between the boiling points of the paraffinic and the aromatic components that is essentially independent of daily variations in column performance. The extrapolation of the aromatic calibration was performed by maintaining a constant distance from the paraffinic curve at retention times greater than 15 min (Figure 13). This assumption was made from the apparent trend of the curve at retention times ranging from 5-15 minutes. With retention time as the common parameter, a relationship was established between the aromatic and paraffinic boiling temperatures (Figure 14). By using this approach, the paraffinic standard, which is ideal for calibration over the entire temperature range, can be run on a daily basis, and the mathematical correction for aromatics can be applied.

One problem with the adopted approach is that the extrapolation of the aromatic calibration is subject to curve fitting manipulation. However, the area of the calibration curve that is most important to the determination of the resid conversion (the vacuum distillation cut point, 566 °C) occurs near the retention time of coronene, which does not require extrapolation. If the actual aromatic calibration curve were to have a greater or lesser slope than predicted, only the boiling point distribution above 566 °C would be in question; the fraction that is predicted to boil below 566 °C is expected to be accurate. Since the same temperature correction is used regularly, comparisons among samples in the high-boiling range are precise.

## Catalyst Screening

In order to ascertain the need to presulfide the dispersed and supported catalysts, to attain a representative high activity, and to select the most effective dispersed catalyst precursor, a series of screening experiments was conducted at 440°C for 60 min using deashed resid from Wilsonville Run 258A as the feedstock. The ultimate analysis for the deashed resid is given in Table 6.

Three hydrotreating catalyst precursors were evaluated: two dispersed organometallics (Molyvan L and Mo naphthenate) and a supported Ni/Mo on alumina catalyst (AKZ0, AO-60). A sample of the AO-60 sulfided ex situ also was prepared for activity comparison. Preparation of this material is described below. Each of the catalysts was tested at the hydrotreating conditions in a single run using the experimental procedures described above for microautoclave work. Catalysts that were not sulfided ex situ also were tested with a pretreatment step (375 °C for 30 min).

The following procedure was used to prepare a ¾ g sample of presulfided AKZO AO-60, beginning with 1/16 in extruded alumina pellets. The as-received sample was ground and sized to -100 mesh, then air dried at 250°C for 8 hr. The dry sample was added to the standard 50 mL batch microautoclave reactor, which was purged with 7.93% $H_2S/H_2$ mixture three times to 2.86 MPa (400 psig). The reactor was charged to 3.49 MPa (492 psig), cold, with the $H_2S/H_2$ mixture, and subsequently agitated at 350 cpm in a heated sandbath for 2 hours at 400°C. The reactor was vented, and recharged to 2.67 MPa (373 psig) with fresh $H_2S/H_2$ mixture, and the two- hour heating/agitation cycle was repeated. In total, this volume would contain 6.0 theories of $H_2S$, where one theory is the stoichiometric amount of $H_2S$ required to convert metals in the catalyst charge from the oxide forms to $MoS_2$ and $Ni_3S_2$, respectively. The dry, black powder was recovered from the reactor without the use of any solvent and stored under dry $N_2$ in a desiccator.

Analysis of the sulfided material showed 1.9 mol $S_{added}$ per mol of Mo, compared with the stoichiometric requirement of 2.26 mol $S_{added}$/ mol Mo, the additional amount (over 2.00) needed due to the presence of Ni. The amount of $S_{added}$ is above the 0.53% S present in the as-received AO-60 sample.

## Catalyst Pretreatment

To ensure Mo contained in the Molyvan L could convert to the active sulfide form, a series of experiments was conducted pretreating a mixture of deashed resid (DAR) produced in Wilsonville Run 258A and Molyvan L for selected times and temperatures, followed by a hydrotreating reaction. These tests were performed in the microautoclaves using standard procedures. Using 2% $H_2S$ in hydrogen to sulfide the Mo, pretreatment time (0, 5 and 30 minutes), pretreatment temperature (300, 340, 375 and 440°C) and hydrotreat time (30 and 60 minutes) were varied. Pretreatment was accomplished by agitating the reactor on top of the hot sand while observing the temperature. At the end of the pretreatment period, the reactor was fully immersed in the fluidized sandbath for the remaining reaction time.

## Recycle Work

To estimate the dispersed catalyst activity after reaction, and its utility for recycle, an experiment was conducted using the Wilsonville deashed resid (DAR). Sufficient Molyvan L to give 1000 ppm Mo overall was added to 10% of the DAR charge. This mixture was reacted at 440°C

for 60 min to simulate the first pass. The gases were collected, the reactor was opened, the remaining 90% of the DAR was added, and the second pass was effected.

In other experiments, the DAR was reacted with Molyvan L (1000 ppm Mo) in a first pass. The products of reaction were distilled to an AET of 566 °C (1050 °F), and the resid was recovered. Fresh DAR and heavy distillate were added to return the reactor feed to 3 g for a second pass with the same 566 °C$^+$ (1050 °F$^+$) and 566 °C$^-$ (1050 °F$^-$) composition as in the first pass. Because of losses in recovering the resid, the concentration of Mo in the second pass was 200 ppmw lower than the first pass. The effect of conversion changes due to this lower concentration is smaller than what can be estimated from available data. Changes in the activity of the recycled Mo were determined assuming there is no change in the reactivity of the recovered and distilled resid containing the recycled catalyst,

Parametric Study

A $2^3$ factorial experiment was conducted to better understand the characteristics and behavior of the filtered first-stage products. Using the results of this study, a simple linear model could be developed and optimum conditions selected for hydrotreatment, maintaining minimum $C_1$-$C_3$ gas yield for a required resid conversion. Three factors were selected for evaluation in the study: time, temperature, and catalyst concentration. The effect of $H_2$ partial pressure was not included in this series; it could be determined subsequently in a few one-variable-at-a-time experiments.

A first-stage product, prepared from Glenharold Mine lignite in one-liter autoclave tests (Runs 8a-LA and 8b-LA) at 350 °C for one hour, was filtered and distilled to produce a master sample of about 60 g, which was subsequently divided into 6 aliquots. The filtrate sample was distilled and found to contain 38.3% 566 °C$^+$ (1050 °F$^+$) resid. The as-received filtrate was also analyzed by SIMDIS and found to contain 40% resid (Figure 15).

Experiments were run in duplicate, using 2 grams of feedstock and Molyvan L (either as received or diluted 1:1 with hexadecane) as the catalyst precursor. The reactor was charged to a total cold pressure of 10.10 MPa (1450 psig) with hydrogen containing 2% $H_2S$ to provide ample sulfur to convert the Mo to its sulfided form. Earlier experiments had shown $H_2S$ present in the product off-gases, and most experiments here gave $H_2S$ concentrations in the 2-3% range. Based on the outcome of the presulfiding study, it had been decided that reactions would be conducted with no pretreatment.

# RESULTS AND DISCUSSION

## SOLUBILIZATION AND PRODUCT CHARACTERIZATION

### MICROAUTOCLAVE TESTS

#### Effect of Different Reaction Variables on Coal Conversion

Solubilization tests were conducted in 45 mL microautoclaves with five different coals of three different ranks, six different residence times, three temperatures, three hydride ion sources, six solvents, and a range of hydride reagent-to-coal ratios, solvent-to-coal ratios, water/dry coal ratios, and reactor charge size. Table 7 gives the ranges studied for each of these variables. Coal weathering, the effect of ash sodium content, and the elevation of reaction pressure by the introduction of nitrogen gas also were briefly explored. A series of tests were made using carbon monoxide (CO) and CO/methanol as solubilization agents for direct comparison to tests made with hydride ion reagent "A".

Coal conversion is dependent on temperature, residence time, coal rank, hydride ion-to-coal ratio, solvent type, solvent-to-coal ratio, and pressure. Coal conversions greater than 90 wt % were obtained by the manipulation of these variables within the ranges given in Table 7. Table 8 is a list of microautoclave tests chosen to show some of the different combinations of values of these variables which produced high coal conversions. The microautoclave test data are presented in Appendix 1.

#### Residence Time

Coal conversion of Black Thunder Mine subbituminous coal and Freedom Mine low-ash lignite was found to be a function of residence time at a given reaction temperature. In the 45 mL microautoclaves, residence time is measured from the time the reactor is placed in the hot sand bath to the time it is removed. Heat-up times are on the order of 74 °C/min and are included in the total residence time reported. The data at ca. 2 min were achieved by heating the reactor to reaction temperature and immediately withdrawing it from the sand bath.

Coal conversion increases with increasing residence time and appears to level off after 60 min in tests made at 350 °C with Freedom Mine lignite (Figure 16). Tests made at 375 °C show a small dependence between 45 min and 150 min, and at 400 °C there appears to be no dependence of coal conversion between 45 and 150 min. In the case of Black Thunder Mine coal (Figure 17), the dependence of coal conversion on residence time at short times (between

2 min and 45 min) is clearly evident. As residence time increases beyond 45 min, the dependence is less pronounced. In the cases of reaction at 375 °C and 400 °C, there is no dependence on residence time at times longer than 45 min.

Tests made with Ohio 11 Mine bituminous coal at 350 °C for 30 min and 60 min show coal conversion to be clearly dependent on residence time. Coal conversion at 30 min was 78.8 wt % and at 60 min was 90.1 wt %.

Reaction Temperature

Coal conversion is strongly dependent on reaction temperature at short (<60 min) residence times and low hydride ion reagent/dry coal ratios. The dependence on temperature becomes less distinct as residence time increases. This is evident in Figures 16 and 17 for tests made with Black Thunder Mine coal and Freedom Mine lignite. Because coal conversion also is dependent on hydride ion reagent/dry coal ratio, Tables 9 through 12 compare coal conversion for Freedom Mine lignite, Black Thunder Mine subbituminous coal, Ohio 11 mine bituminous coal, and Glenharold Mine lignite at varying reaction temperatures with constant hydride ion reagent/dry coal ratio and residence time. As hydride ion/dry coal ratio or residence time increases, coal conversion at 375 °C is equal to or greater than that obtained at 400 °C. This maximum conversion at intermediate temperatures has been observed in work done previously at CONSOL. It may be an indication of retrogressive reactions occurring at the higher temperature.

Heating Rate

Several experiments were conducted with slow heating rates (1 °C/min and 2.5 °C/min) followed by different residence times at the final temperature of 350 °C (Figures 18 and 19). The coal conversions, obtained with both Freedom Mine lignite and Black Thunder Mine coal, from these tests were no different than those obtained from rapid heating followed by the same residence times. Thus, the slower heating rates that were used in one-liter-scale reactions (see below) are not expected to influence coal conversion. In fact, coal conversions in the one-liter system were comparable to corresponding microautoclave tests (see below).

Hydride ion reagent/dry coal ratio

The ratio of hydride ion reagent to dry feed coal was studied. Coal conversions are poor without hydride ion reagent at reaction temperatures of 350, 375, and 400 °C. In Figures 20 through 22,

these values are represented by points on the 0 hydride ion reagent/dry coal axes. In the case of Black Thunder Mine coal at a reaction temperature of 350°C, as the ratio is increased coal conversion increases. At other reaction temperatures and with other coals (Figures 21 and 22), the increase in coal conversion plateaus at ratios of about 1/1. Hydride ion reagent/dry coal ratios greater than 1/1 are not very effective in improving coal conversion.

Autogenic Pressure

System pressure at reaction temperature was calculated by summing the calculated steam pressure and permanent gas pressure determined at reaction temperature. The void volume of the reactor was determined by assuming all hydride ion reagent and water would be vaporized at reaction temperature. Steam pressure was determined from the total weight of water in the reactor (coal moisture plus any added water). Pressure of permanent gases was determined using the ideal gas law from the gas pressure measured at room temperature.

The system pressure is strongly influenced by the water loading in the reactor, reaction temperature, and void volume. Manipulation of all three of these variables was done to alter the total system pressure. At constant temperature, coal conversion increases as system pressure increases (Figures 23 through 25). Within a total pressure range of 1000-4000 psi, coal conversions increase 15-20 wt % (absolute). Increasing the system pressure by the introduction of $N_2$ to the reactor prior to testing does not improve coal conversion, even when the system pressure at reaction temperature is equivalent to, or greater than, that obtained by the addition of water (Figure 26).

Hydride Ion Reagent

Three hydride ion reagents, designated HI "A", "B", and "C" were studied in Task 2. Comparison of coal conversions obtained using the different hydride ion reagents under similar reaction conditions is given in Tables 13 and 14. Economic considerations will influence the choice of hydride ion reagent for a large-scale liquefaction facility (see Engineering and Economic Evaluation, below). Because HI "A" is expected to be the least costly to use, attention was primarily focused on its use in Task 2. Other potential sources of hydride ion include $CO/H_2O$, $CO/MeOH/H_2O$ added, CO/MeOH, and hydride salts. Preliminary investigations were made with $CO/MeOH/H_2O$ systems in Task 2 (see below).

Solvent Type

Six solvents were used in microautoclave tests. The solvents are a Wilsonville Two-Stage Coal Liquefaction Pilot plant recycle oil (V1074) from Run 262 period E; the 488°C$^-$ distillation cut of that oil; a pasting solvent distillate from the Lummus pilot plant (Run 3LCF7); two anthracene oils (one from Reilly Industries and the other from Kawasaki Steel Corporation); and tetralin. Analyses of the coal-derived oils are given in Table 2. Proton NMR spectroscopy data are given in Table 3.

Tests made with Freedom Mine lignite for 60 min at 350°C, HI "A"/dry coal = 1.1 and a constant solvent/dry coal = 2.2 show an influence of solvent type among the coal-derived solvents (Table15). Coal conversion (about 72 wt %) for tests made with Wilsonville Run 262E V1074 distillate as solvent was similar to that obtained with the whole Wilsonville solvent. Coal conversion obtained with the pasting solvent dstillate from Lummus Run 3LCF7 was similar (75 wt %). However, a test made with Freedom Mine lignite and Reilly Industries anthracene oil gave a coal conversion 10 wt % higher than the conversion obtained with the Wilsonville distillate solvent. Coal conversion is about a 7 wt % lower when tetralin is used.

Tests were made with Glenharold Mine lignite and all five-coal-derived solvents at 350°C, 60 min, HI "A"/dry coal = 1.0 and solvent/dry coal = 2.0 (Table 15). The pattern seen with the Freedom Mine lignite was repeated with the Glenharold lignite. Coal conversions are higher in the more aromatic Lummus solvent and anthracene oils. However, the effect is much larger with the Glenharold lignite than it is with the Freedom Mine lignite. Coal conversions increases 15-17 wt % with the more aromatic solvents. The difference between the Wilsonville solvent and the aromatic solvents is more evident as the solvent/dry coal ratio is increased (see below). The effect of solvent type was further explored with Black Thunder Mine subbituminous coal at 350 °C, 60 min with HI "A"/dry coal = 1.0 and solvent/dry coal = 2.0 (Table 15). Coal conversion are about 18 wt % higher with anthracene oil than with the Wilsonville solvent (84 vs 66 wt %). Coal conversion for a test made with the Lummus solvent was intermediate at ca. 74 wt %.

Improved solubility of the first-stage product in the more aromatic oils (the Lummus solvent and the anthracene oils) is considered to be the likely reason for the higher conversion. It is believed that the Wilsonville solvent, because of its high paraffinic content is unable to disperse the first-stage solubilized coal product when it is made under low severity conditions. It can be speculated that, as the product is formed and solubilized, there would be created a driving force

to form more product. Thus, increased conversion would be obtained in a solvent that would be more like the first-stage dissolution products obtained at the low-severity conditions. Additionally, as the aromatic products are solubilized in the solvent, it would be less likely that there would be retrogressive reactions occurring. This is supported by filtration studies with first-stage product made with Glenharold coal at 350°C, 60 min, in Wilsonville 262E solvent. These first-stage products would not completely resolubilize in the Wilsonville V1074 solvent at temperatures as high as 300°C, but readily solubilized at 150°C in a high-boiling aromatic coal tar distillate.

Six microautoclave tests were made to test the use of recycled solvent (Table 16). Conditions were the same as those used for five microautoclave material balance tests made throughout Task 2 (see below). Solvent recovered from the one-liter autoclave test Run 8-LA (see below) rather than virgin Wilsonville Run 262E V1074 was used. Coal conversions for the tests made with Black Thunder Mine subbituminous coal are on average 1.5 wt % (abs.) lower than those originally obtained. Coal conversions for the test which used Ohio 11 Mine bituminous coal was 0.5 wt % (abs.) lower than for the corresponding test made with the virgin solvent. Coal conversion for the test which used Glenharold Mine lignite was about 8 wt % (avg.) lower than the average conversion from previously made tests which used the virgin solvent. The recycled solvent was shown by GC/MS analyses to be even more paraffinic than the virgin material. This seems to support the concept that the more aromatic the solvent, the better will be coal conversions.

Solvent/Dry Coal Ratio

Solvent/dry coal ratios were altered in Task 2 primarily to adjust the total reactor loading. Comparisons made of microautoclave tests in which all other factors were held constant indicate that there is little effect on coal conversion from altering the ratio of solvent to dry feed coal when the ratio is above some threshold. With Wilsonville 262E V1074 distillate solvent and Black Thunder coal, that threshold appears to be at most 2.4 (Table 17).

In the case of Glenharold coal, the more aromatic Lummus pasting solvent was a more effective solvent than the Wilsonville Run 262E V1074 distillate when the coal was solubilized at 350°C for 60 min at low (1.5 or lower solvent/dry coal ratios). Microautoclave tests made with Glenharold Mine lignite and Wilsonville Run 262E V1074 were made with varying solvent to dry coal ratios (Table 17). Coal conversion decreased with decreasing ratios. Substituting Lummus

Run 3LCF7 pasting solvent distillate for the Wilsonville solvent resulted in high coal conversions at all solvent to dry coal ratios tested. The aromatic content of the Lummus solvent is believed to be important for solubilizing the first-stage product (see above).

The impact of solvent to coal ratio on interstage filtration was explored using first-stage products generated at three different solvent/dry coal ratios (2.0, 1.5, and 1.0). Although the filtration rate was slower at the lower solvent/dry coal ratios used, because of the higher solids content, the overall filtration rate was constant (see Filtration, below).

Coal Weathering

The effect of coal weathering on coal conversion was briefly explored and found to have a negative impact on coal conversion. Samples of Black Thunder Mine subbituminous coal were artificially weathered by holding them in a 100 °C oven for 14 days (Table 18). Microautoclave test conditions were 350 °C, 60 min, HI "A"/dry coal = 1.5, solvent/dry coal = 2.4, total reactor loading 17.5 g and 22.5 g. Coal conversions were 61.0 and 66.2 wt %, respectively, with the weathered coal and 77.4 wt % coal conversion and 81.8 wt % with fresh coal. No further study of coal weathering effects was made.

Sodium Content

The sodium content of the feed-coal was briefly investigated using high-ash, high-sodium, and low-ash, low-sodium-content samples of Freedom Mine lignite. Coal conversion was lower with the high sodium coal (Table 19). The high-ash, high-sodium-content sample of Freedom Mine lignite was determined to have 8.2 wt % $Na_2O$ on ash content (Table 1). Microautoclave tests made with this coal at 350 °C for 45 min and 60 min gave coal conversions ca. 7-8% poorer than those obtained with the low-ash, low-sodium-content Freedom Mine lignite.

It generally was concluded that sodium is not influential in achieving high coal conversions with lignites and high coal conversions of high-sodium-containing coals can be obtained..

Sodium as Catalyst

A review of the factors which influence coal conversion described above (time, temperature, and hydride ion reagent concentration) indicate that the limitation on coal conversion at the lowest temperature, lowest hydride ion reagent/dry coal ratio, and shortest time may be kinetic. To test the potential of sodium as a catalyst for the promotion of high coal conversion in the first-stage

reaction, sodium was introduced into the low-ash Freedom Mine lignite reaction system by two methods: a sodium salt of a hydride ion reagent (Hydride Ion Reagent “C”) was added in the crystalline form to dry coal and an aqueous solution of the reagent was added to the reactor or to the coal charge (Table 20). The addition of sodium as the salt to the reaction system at the addition rates tested produced no change in coal conversion as compared to the starting Freedom Mine lignite and HI "A".

Mass and Elemental Balance

Mass and elemental balance data (Tables 21) were obtained for three microautoclave tests made with Black Thunder coal, one made with Ohio 11 Mine bituminous coal, and one made with Glenharold Mine lignite.

Mass balances for the five tests were good (95.4% to 100%). Carbon balances obtained were 86.6% to 100% and hydrogen balances were 95.2% to 103%. Product component distributions given in Table 21 indicate that essentially all of the solvent used in the process is recovered as the 120-488 °C distillate. Gas makes are ca. 14 to 16 wt % of the feed. This is directly related to the choice of hydride ion reagent. The economic implications of conversion of a large percentage of the reagent to gas are discussed below (see Economic and Engineering Evaluation). In the microautoclave mass balance tests no evidence of unreacted (or reformed) hydride ion reagent was found in the reaction products. This is not the case in the one-liter mass balance tests (see below). The amount of product which is THF-insoluble, and would presumably be separated from the feed to the second-stage reactor by the filter is between 3.5 and 5.5 wt % of the feed; of that, 1 to 2 wt % is ash. Therefore, loss of feed coal with ash rejection would be about 2 wt %.

Comparison to $CO/H_2O$ Coal Liquefaction Process

Task 2 investigations included a series of microautoclave-scale tests made with carbon monoxide (CO), four different coals, and solvent. As can be seen from the data in Table 22, increasing the molar quantity of CO in the reaction system with all other variables held constant results in increased coal conversion. There also is found a dependence of coal conversion on residence time when CO is present in the reaction system. Each of these findings parallels results obtained in Task 2 using hydride ion reagent "A".

Coal conversions obtained with CO are much lower than those obtained with HI "A". As shown in Table 23, coal conversions obtained using CO are 19 to 33.6 wt % (abs.) lower than those obtained using HI "A" at the same residence time (60 min) and temperature (350°C) and with the same molar quantities of CO as HI "A".

The addition of methanol in equimolar concentration to CO to the CO reaction system improves coal conversion. However, coal conversions in the CO/MeOH system under the same reaction conditions are not as high as when HI "A" is used (Table 24).

The literature[6-23] was examined for conditions and maximum coal conversions in $CO/H_2O$, $CO/H_2$, and $CO/H_2O$/catalyst systems. High coal conversions (>90 wt %) are reported; however, they are generated only either at high temperatures (>400°C) or in the presence of catalysts (Table 25). This implies that the mechanism used to obtain the high conversions in the hydride ion reagents at low temperature may be different than that undergone by the $CO/H_2O$ reaction system.

## ONE-LITER AUTOCLAVE TESTS

One-liter stirred autoclave tests were made in Task 2, primarily to produce large quantities of material for interstage filtration and second-stage hydrotreating studies. Work with the one-liter autoclave in Task 2 provided experience for the integration of the first-stage reactor and the interstage filter, which is to be done in Task 3. The one-liter autoclave test data are presented in Appendix 2.

In Task 2, tests completed in the one-liter autoclave are replicates of 45 mL microautoclave runs (Table 26). One-liter autoclave tests were made with Black Thunder Mine subbituminous coal, Ohio 11 Mine coal, Freedom Mine high-ash-content lignite, and Glenharold Mine lignite. All tests made in the one-liter autoclave used solvent and HI "A". Four tests were made with water added to the reaction system.

The influence of slow heat-up and cool-down times was addressed in the microautoclave study (see above). In the one-liter tests conducted under Task 2, the heat-up and cool down profiles for all tests are the same. A representative profile is shown in Figure A2-1. System pressure in all runs was strongly influenced by the addition of water to the reaction system (see Appendix 2). System pressures were between 2650 and 3860 psig.

## Coal Conversion

Coal conversions for one-liter autoclave Runs 4-LA, 4B-LA, 5-LA, 6-LA, and 7-LA were calculated from THF-solubilities of grab samples (Table26). The coal conversions for Run 8-LA and 9-LA were obtained by pressure filtration in THF of the entire 120 °C$^+$ fraction. Coal conversions are within 3 wt % (absolute)of corresponding microautoclave test results for all but Run 4B-LA which was 5 wt % lower than the corresponding microautoclave test.

## Alternative Product Recovery

The one-liter autoclave test Run 7-LAwas successfully completed using the Method 2 recovery procedure (see Experimental). In this procedure, the hot contents of the autoclave are transferred at the conclusion of the run to the receiver vessel located directly under the autoclave. After transfer, the entire system wascooled and gases were collected as in previous tests. After the run the autoclave was opened; the walls of the autoclave had only a film of material left on them. The procedure, as executed, provides necessary experience for installation of a filter between the reactor and the receiver vessel in Task 3.

## Mass and Elemental Balance

Mass balances were obtained for a number of one-liter autoclave tests. Mass recoveries were 85.1% to 97.8%. An elemental balance was obtained for Run 8-LA which used Glenharold Mine lignite (Table 27). Coal conversion in Run 8-LA was 93.4 wt %. The productdistribution from Run 8-LA shows an 8.7% gas make; this is related to the choice of hydride ion reagent, as was the case with the microautoclave tests. Almost all the solvent is recovered.

In the IBP-120 °C fraction of Run 8-LA products, unreacted hydride ion reagent was recovered. No hydride ion reagent was recovered from corresponding microautoclave tests. Quantitation of the hydride ion reagent remaining in the reaction system is difficult because of its high volatility. Work under Task 3 will address quantitative recovery of the reagent.

Test conditions for Run 8-LA were 60 min, 350 °C, HI "A"/dry coal = 1.0, solvent/dry coal = 2.4. Water was added to the reaction system. These conditions were chosen for the production of a single large sample for filtration and second-stage catalytic upgrading studies (see below). Three additional one-liter tests (Runs 8a-LA, 8b-LA, and 8c-LA) were made under the same conditions to produce the large sample.

One-liter autoclave tests Runs 9-LA and 9a-LA were made with Glenharold Minelignite, Lummus 3LCF7 pasting solvent and hydride ion reagent "A". Reactor temperature was 350°C for 60 min. Solvent/dry coal ratio was 2.4 for Run 9-LA and 1.5 for Run 9a-LA. Run 9-LA was a material and elemental balance test and Run 9a-LA was made to produce sample for subsequent filtration and second-stage catalytic upgrading studies. In Run 9-LA a total mass recovery of 94 wt % was obtained. Losses are presumed to be of the unconsumed hydride ion reagent and its volatile byproducts. Coal conversion was 93 wt %. Gas make was approximately 11 wt % (on a feed basis).

## FIRST-STAGE PRODUCT CHARACTERIZATION

### Elemental Analyses

Elemental analyses of the 488 °C$^+$ products of six first-stage reactions are presented in Tables 28 and 29. These are the products of the mass and elemental balance microautoclave tests Runs 74, 74b, 76, 117, and 127b, and one-litertest Run 8-LA. In each case, the first-stage product is enriched in hydrogen over the feed coal. The H/C ratios for each of the products are greater than that of the corresponding feed coal. The sulfur content of the 488°C$^+$ products is reduced to less than half that in the coal in all cases.

Comparison of the O/C molar ratios show the products of the Black Thunder Mine subbituminous coal and the Glenharold lignite are substantially depleted in oxygen from the feed coals. The O/C ratio for the Black Thunder Mine coal products is one-third to one-half that of the feed coal. In the case of the Glenharold lignite, the O/C ratio also is reduced to one-third of the feed coal. The products of the Ohio 11 Mine bituminous coal, which has a relatively low oxygen content, have an O/C ratio similar to the feed coal.

### Solvent Fractionation

Six 488 °C$^+$ product samples were subjected to solvent fractionation by methods described in *Fuel* 1979, *58*, 539-541. The samples are the 488 °C$^+$ fraction of the first-stage product of Runs 73, 74B, 76B, 127, and 143, which were made in 45 mL microautoclaves, and Run 8-LA, which was made in a one-liter stirred autoclave and used the same conditions as Run 127B. The yields of 488 °C$^+$ fraction and the oils, asphaltenes and preasphaltene of that fraction are reported on a MAF coal feed basis (Table 30). From these analyses, it can be generally concluded that higher reaction temperatures and higher solvent-to-dry-coal ratios result in a higher oils content of the 488 °C$^+$ fraction.

Filterability

A number of products of the first-stage solubilization reaction were subjected to filtration (see below).

## FILTRATION

### APPROACH

Initially, small samples (10g) from first-stage microautoclave tests were available for filtration tests. A small filtration rig was designed and built to cope with these very small samples. The aim was to get sufficient information to assess whether these novel feedstocks were easy or difficult to filter. These initial tests were followed by a study of a range of filtration parameters when first-stage 1 L autoclave products became available. A large filtration rig was assembled for these studies and to provide filtrates that were concentrated by vacuumdistillation prior to upgrading (see below).

A summary of the Task 2 filtration experiments performed on first-stage products is provided in Table 31. Tables 32 to 35 summarize the mass balance data, where available, and give a summary of the filtration data for the four coals used. In Tables 36 to 38 the characteristics of the feedstocks and products of filtration are shown with some analysis of process parameters for optimized operation.

### EFFICIENCY OF SOLIDS REMOVAL

Regardless of the type of filtration medium used, glass fiber papers (1 µm particle size retention) or Conidur (100 µm x 500 µm aperture), the efficiency of solids removal from the first-stage products was very high for all size particles to at least the micrometer level. This conclusion is based upon:

- No visible signs of failure of the sealing system around the filter media
- SEM observation of the filter cake in which micron sized particles can be seen along with the larger coal and mineral matter fragments (Figure 27)
- SEM observation of the material which was collected during the refiltration of the filtrates after dilution with THF, which indicated that any material so collected was formed by the precipitation of coal extract in the added solvent, i.e., not all the coal extract that was in solution at filtration temperature was soluble in THF (Figures 28 and 29)

The THF insolubles (THFIs) only contained traces of ash components, sulfur being the major non-carbon element detected by energy dispersion analysis by X-ray excitation (EDAX). Because of the very small quantities available,no full ash analyses were possible. (It should be noted that if particles had by-passed the filter to contaminate the coal solution, the composition of solids collected in the second filtration would be expected to be around 50% ash, and this would have been apparent in the EDAX examination).

The high efficiency of solids separation achieved is tobe expected when using glass fiber as the medium; however, such a screen is not practical for a large industrial plant. The performance of the Conidur screen with orifices that are much larger than the particle size of the feed coal and the fragmented coal after liquefaction was, thus, very encouraging. The bridging of the 100 µm gaps must have occurred very quickly. For example in NCF 43 (Table 31) (Glenharold Mine lignite, Lummus solvent) the filtrate was collected in batches. The first filtrate sample, representing the first 20% of the total filtrate (~5 mm of cake) had a THFI content of only 0.16%. All later samples had THFI's of less than 0.1%. Some of these insolubles may have been precipitate and not undissolved coal particles. As a demonstration of this fact, onesample of coal solution (NCF 34 and 35) containing 8.2% material insoluble in THF was assessed for solubility in quinoline and found to contain only 0.9% insolubles (QI). Thus, about90% of the THFI was soluble in quinoline, and a maximum of 10% were solids. From this, it may be inferred that the amount of particulate materials passing through the Conidur screen is probably below 0.1% at the start (0.01% if the above ratio for THF/QI is applied) and overall will be much lower as the cake builds up and controls ultimate particle retention.

Determination of the ash content of several filtrate samples show that a significant amount of material that eventually will form ash had passed through the filter media. SEM and EDAX examination of the ashed filtrates indicate that it consists, in most casesof principally Ca and S with only traces of the other common coal ash components (Figures 28 to 30). This ash in the filtrate is concentrated in the heavy part of the coal extract. In samples 8ab-LA and 8c-LA, the light fraction had the lower ash content (0.18% and 0.08% of the 566 °C-, compared with 2.7% and 2.3% for the heavy fractions (Table 36 and Figure 31). The ash in the filtrates represents up to 1% of the dry coal (10% of the coal mineral matter).

It is well known that high calcium coals can cause problems in coal liquefaction plants due to deposition of calcium salts within the reactor. These salts can form "nodule" growths and, if

allowed to pass into a catalytic upgrading unit, deposit on the catalyst support. By varying reactor conditions and process configuration, it may be possible to remove these materials with the filter cake. This aspect will be studied during Task 3. It should be noted that in the LSE process, "ash" removal efficiency improved during recycling and that filtration rates improved.[24] These two facts led to the conclusion that a small amount (less than 2% on coal) of heavy extract which included ash precursor was precipitating and causing ash agglomeration (hence faster rate). By calculation, 5-10% (on dry coal) of heavy extract precipitated and left behind with the filter cake would give an ash removal of over 99%, (Figure 31). An alternative route out of the plant for this "soluble ash", if it can be allowed into the upgrading stage, would be along with the aged catalyst and its associated pitch. It might be possible to direct this bleed stream back to the filtration section, either directly or via the first stage and eventually reject all the ash and catalyst with the filter cake. This route was shown to be feasible.[25]

## EFFECT OF COAL TYPE

Products of four coals were filtered during Task 2: Freedom Mine lignite, Glenharold Mine lignite, Black Thunder Mine subbituminous coal, and Ohio 11 Mine bituminous coal.

### Freedom Mine Lignite

High filtration rates were a feature of all of the micro filtration tests using first-stage products prepared from Freedom Mine lignite. Some were too fast to measure the rate. Reducing the filter temperature to increase the viscosity (with the aim of obtaining flow rates that could more easily be measured) was precluded, since this also could result in further precipitation of the dissolved coal. In the tests where measurements were possible, the data were interpreted in terms of constant rate filtration. Very low cake resistivities (1-2 x $10^{10}$ m/kg) and high total flows (>150 kg/$m^2$ of filter area) were determined after 30 min, Table 32. The larger sample from the one-liter autoclave test, Run 7-LA (NCF 22), was the exception. The behavior of this sample in the 200 mL filter unit was more like classic filtration. There was some indication of two-phase flow (a noticeable change in flow character part way though the test). The yields of filter cake reflect the differences in conversions achieved at increasing reaction temperature, ranging from 350 to 400 °C (Table 31). Similarly, the viscosities follow the same trend, increasing as more coal is extracted at the higher reaction temperatures (Figure 32). The high viscosity of the filtrate from test NCF 22 was estimated from a softening point determination and should be treated with caution.

Conversion yields were calculated from two different routes: (1) mass balance data and the determination of the IOM in the filter cake (using THF as the solvent), and (2) ash enrichment calculations based upon the ash content of the feed coal and the filter cake. Good agreement between the methods was obtained. Conversion yield was shown to increase from ~70% to ~90% as the first-stage reaction temperature was increased from 350 to 400°C (see above).

Glenharold Mine Lignite

The first-stage product samples that were made using Glenharold Mine lignite (Runs 8a-LA, 8b-LA, 8c-LA, and 9a-LA) and subsequently filtered were produced in the one-liter autoclave (see above). Attempts to reconstitute the combined sample from Runs 8a-LA and 8b-LA by blending the appropriate amounts of the separated lights and heavies were not particularly successful. Transfer of the 'blend' from the mixing vessel to the filter invariably resulted in a disproportionate amount of the heavy fraction being left behind in the mixing vessel. In addition, the filtration tests were virtually instantaneous and too fast to measure. The data from these tests, NCF 28 - 32, could not be processed to give reliable information. Filtration of the heavy fraction alone was accomplished in NCF 37. A low cake resistivity based upon an estimated viscosity (from softening point determination) and a high total flow at 30 minutes, 290 kg/m$^2$, were achieved, Table 33.

With products of Run 8c-LA, filtration of the heavy fraction, NCF 34 and 35, was more difficult due to the very high viscosity of this material (>3000 mPa•s). Blends were made with a heavy coal tar distillate (CTD). Viscosities fell to a workable range for all of the blend ratios. The form of the flow-rate plots (and its inverse) showed little evidence of two phase behavior. This behavior is more typical of a well-dispersed, uniformsuspension. Cake resistivities were similar to those found for other coal liquids,[26] 50-100 x $10^{10}$ m/kg. The total flow at 30 min fell progressively from 80 to 20 kg/m$^2$ with a decreasing content of coal tar distillate in the blend from 60% to 25%.

In test NCF 42, the differential pressure across the filter was doubled from 0.1 MPa to 0.2 MPa part way through the test in order to determine the compressibility of the filter cake. Unfortunately, the data obtained during the higher pressure phase of the test are too scattered to give a reliable value for the cake resistivity. However, a best estimate suggests that the compressibility lies in the range 0.3 to 0.6. Better data from a systematic study on a single feedstock is required. Distillate from a previous batch of filtrate was used to wash this cake

before it was vacuum dried. The flowrate data show the expected increase in rate as the lower viscosity wash solvent replaces the coal solution in the cake, before settling out to a uniform higher rate.

The filtration plots from Run 9a-LA (NCF 43) followed the classic form as defined by Darcy's equation (Figure 33). This first-stage product, made using Lummus pasting solvent, required no separation prior to filtration. It had a low viscosity and a higher cake resistivity than products of Run 8c-LA / CTD blends. Total flow at 30 min was 93 kg/m$^2$. The coal conversions from ash enrichment calculations were 90-95%.

Black Thunder Mine Subbituminous Coal

The data from the filtration tests made with first-stage products of Black Thunder Mine subbituminous coal follow very similar trends to those from the lignites (Tables 32 and 34). Filtration of the products from the microreactor tests were all analyzed in terms of constant rate filtration. Flow rates were very high resulting in low cake resistivities and high total flows at 30 min, >100 kg/m$^2$. Results were calculated from an assumed value of the viscosity of 1 mPa•s.

Conversion yields calculated by the two methods (described above) were in good agreement. The yields increased as the first-stage reaction temperature was raised from 350 °C to 400 °C. The conversions calculated for the one-liter autoclave tests, Runs 4-LA and 5-LA, are suspect and are likely associated with problems experienced in obtaining reliable mass balance data for these tests.

Ohio 11 Mine Bituminous Coal

Table 35 gives the results for the microautoclave tests using Ohio 11 Mine bituminous coal. The properties of the first-stage products made from it are somewhat different than those made from lignites and subbituminous coals. No attempt was made to filter the sample (Run 123), which was prepared at 300 °C (Table 31). This sample had the consistency of a dry powder at room temperature. Bituminous coals in low temperature liquefaction soften, swell, and absorb the solvent. Under the applied pressure in a filter cake, these partially extracted coal fragments deform to severely inhibit flow through the cake. A longer reaction time (and higher temperature) allows the depolymerizing process to proceed to completion, leaving more rigid particles that

facilitate filtration. In contrast, lignite derived coal-liquefaction products do not behave the same way.[27]

The other samples prepared from Ohio 11 Mine coal at reaction temperatures from 370°C to 400 °C were filtered successfully. All tests except NCF 27 (Run 128) were classed as constant rate filtrations like the lignite-derived samples. For these bituminous coal-derived first-stage products, the viscosities were substantially higher and could only be estimated from softening-point determinations. The cake resistivities were similar to those for Glenharold Mine lignite products, decreasing as reaction temperature was increased. The total flow at 30 min mirrored the cake resistivity, increasing from 20 to 100 kg/m$^2$ with increasing reaction temperature.

Coal conversions calculated from the ash enrichment were consistently high (~95%) throughout the first-stage reaction temperature range. There was a lot of scatter from the mass balance calculated conversions, attributed to some spurious cake THFI determinations.

## FILTRATION TEMPERATURE AND PRESSURE

The range of filtration temperatures that could be used is limited at the lower end by the precipitation of coal extract from solution. The amount of such precipitation depends primarily on the solvent (diluent) and extract compositions. The first-stage products are highly aromatic and of high molecular weight. In many instances the diluent was aliphatic in nature and found to be incompatible with the coal extracts (see “First-Stage Solubilization Solvent Type”, above). Solubility increases with temperature; therefore, even with the more aromatic diluents used, it is advantageous to filter at as high a temperature as practical.

At solvent-to-coal ratios used in the first-stage reactions, there is a significant reduction in viscosity as the temperature increases from 200 °C and 300 °C. This indicates that there is an advantage in using as high a temperature as possible. However, the expected increase in flow rate resulting from a reduction in viscosity as temperature is increased is not necessarily realized in practice due to the dependence of cake resistivity on temperature. Thus, the improvement in rate at lower viscosity is offset by the increase in cake resistivity.

The construction of the filter and the associated downstream pressure will limit the filtration temperature. The pressure will depend upon the boiling range of the recycle diluent chosen. A

downstream pressure of 4 bar at 300/330°C would be appropriate. The single measurement of cake compressibility that was made (see above) was similarto that from Black Thunder Mine coal tests under ITSL conditions,[28] i.e., a 50% increase in rate between 0.1 MPa and 0.2 MPa pressure differential. Therefore, the use of pressure differences less than 0.8 MPa are recommended.

## RECOVERY OF PRODUCT FROM FILTER CAKES

### Cake Washing

One experiment was performed which indicated that the extract could be recovered from the filter cake by washing. Because of the relatively low content of extract in the first-stage product filtrates and the low solids concentration, there is little economic incentive to wash the filter cake. The reduction in rejected hydrocarbons with the IOM is likely to be only about 2% (on dry coal basis). Lowering the solvent-to-coal ratio in the first stage may influence the need to wash the filter cake.

### Vacuum Drying

A single test in which a washed cake was vacuum dried in situ at 1.3 kPa (10 mm Hg) and 300 °C showed that within experimental error all the distillate solvent could be recovered from the filter cake. These are conditions that could be applied to the filter at the end of the filtration step without the need for any further heat transfer to the filter cake. This could be achieved commercially with a large filter. Previous experience both at the Wilsonville pilot plant and by British Coal would suggest that vacuum drying the filter cake in situ will give virtually the same distillate recovery as in the laboratory test and produce a filter cake with ca. 90% solids.

### Nitrogen Blowing

Gas blowing of the filter cake at the end of the cake formation period was effective in removing some of the liquid wetting the cake. Towards the end of filtration, there is a period when gas breakthrough has occurred and liquid flow/cake drainage is incomplete. An advantage of gas blowing is that it helps to force the whole liquid phase through the filter cake. However, as blowing proceeds, there will be a greater proportion of liquid in the vapor phase. If vacuum drying is to be included in the filtration cycle, it is probably better to terminate gas blowing as soon as extract ceases to appear in the blowings (filtrate). In practice, an industrial filter with vertical leaves or candle elements can be blown with nitrogen for an average of 1-2 min during

draining of the filter body (at the end of filter cake formation) without impacting on the overall cycle time or the filtration cost.

Filter Cake Density

Knowledge of the density of the filter cake is important in designing large units since the filter element spacing depends upon the volume occupied by the filter cake, plus a safety allowance. If the cake is allowed to entirely fill the space between filter elements, hydraulic forces can severely distort the filter element.

The cake densities calculated for most runs are shown in Figure 34. In most cases, particularly in the microfiltration rig, cake thickness were only a few mm, and the cakes did not have perfectly flat surfaces. An exception is run NCF 43 in which the cake was 25 mm thick. The cakes, as formed with all their pores full of liquid, have a density of about 1.4 g/mL (1400 kg/m$^3$). This reduces to around 1.0 ± 0.1 g/mL when these wet cakes were drained and blown with gas. The cakes have only about 50% solids based upon THF solubility measurements. Therefore, the density of the solids (IOM and mineral matter) was about 0.5 g/mL. The solids content of the cake formed is thus only about 35% on a weight basis. This agrees with the true densities of the individual components (1.5 g/mL for coal and IOM, ~3 g/mL for ash, and 1 g/mL for coal solution or filtrate). The cakes, as formed, could consist of:

| | | |
|---|---|---|
| 66% | coal solution contributing | 0.66 g/mL |
| 17% | ash contributing | 0.51 g/mL |
| 17% | IOM contributing | 0.25 g/mL |
| | giving an overall density of | 1.42 g/mL |

Filtration of a slurry of unreacted coal in solvent (NCF 1) gave a cake of density 1.9 g/mL reducing to 1.34 on a THFI basis. This illustrates the lower packing density and/or greater porosity of the IOM particles compared to pulverized raw coal, particularly when the much lower ash content in the coal is allowed for (i.e., 10% compared with these filter cakes at 50%).

Shrinkage of the cakes occurs during cooling, which form cracks in the cake. This is not unexpected as the cakes, as formed, are mainly liquid which could shrink by around 20% on cooling from filtration temperature of 300 °C to room temperature.

## FILTER MEDIA PERFORMANCE

### Bridging

As intended in initial tests, the micro filtration rig utilized glass fiber filter papers with a rated retention of 1 µm. It had not been planned to test coarser, more commercially practical screens until the large batch of feedstock became available so that comparison of various media would be made with the same feedstock. This was to be used in a systematic series of tests, which included the comparison of the performance of various filter media using a common feedstock. However, the initial tests with bituminous coal gave very slow filtration rates, so a coarse screen was tested to determine whether blocking of the pores of the glass fiber papers was to blame for the low rates. A Conidur screen with 100 x 500 µm apertures gave virtually the same flow rates as the filter paper. There is virtually total removal of solids from the feed material (at least down to the sub micron level) with the Conidur screen. Thus, although the very first particles approaching the Conidur screen have a chance of getting through into the filtrate, the solids bridge across the 100 µm orifices and the filter cake itself becomes the filter medium controlling particle size retention.

### Blinding

Each time the Conidur filter screen was used, the cold cake was easily removed. There was only minimal blocking (i.e., less than 10%) of the orifices when viewed optically (by light transmission). This test is obviously not the same as the practical situation when a hot (300 °C) cake is discharged after vacuum drying. However, it is an encouraging result and is probably helped by the type of Conidur used here, which had a smooth upper surface.

## DISTILLATION OF FILTER FEEDSTOCK

The removal of some vehicle solvent after the first stage and before filtration may be economic in terms of reducing the filter size. The viability of including such an operation depends upon the viscosity of the first stage product (after flashing) or, more explicitly, the relationship between the viscosity and the extract concentration in the distilled product. As part of an exercise to investigate the effect of solvent composition (aromaticity) on coal solution stability, a number of experiments were carried out in which a proportion of the Wilsonville solvent was replaced by varying amounts of a heavy coal tar distillate. As a consequence, the viscosity of the resultant coal solution was similarly varied. The filtration data so obtained (runs NCF 34-36 and NCF 39-42) enabled a good assessment to be made of this particular combination of coal and vehicle solvent for a single set of reaction conditions.

It is possible to deduce the optimum effective solvent to coal ratio. The average rate of filtration over 30 min (Table 33) in most cases was calculated by extrapolating the experimental data. These values are multiplied by the appropriate concentration factor to give relative sizes of filters for the same product throughput (the value for neat Run 8c-LA heavies is estimated assuming a compressibility factor of 0.7). The optimum dilution is one part of diluent per one part of 8c-LA decant bottoms. Assuming that the added diluent has the same properties as the original carrier solvent mixture, and knowing that 8c-LA decand bottoms consist of roughly equal quantities of 566 °C$^+$ extract and 566 °C$^-$ solvent (NCF 34 and 35), the optimum solvent to coal ratio would be just under 1.5:1 (Figure 35).

Increasing the filtration temperature and thereby reducing viscosity would shift the optimum solvent-to-coal ratio down slightly. At the proposed conceptual filtrate temperatures of 300/330 °C, a solvent-to-coal ratio of 1:1 might be optimal. However, such filtrate would be only about 30% 566 °C$^+$ and could be distilled to give a more concentrated feed for upgrading. Concentration of the filtrate to 100% 566 °C$^+$ would not be advantageous. This material would not soften until ~300 °C (Table 38); thus, it could not be pumped. The overall flow sheet shown in Figure 36 includes flashing prior to filtration.

At the optimum solvent-to-coal ratio the filtration rate was 64 kg/m$^2$ in 30 min (equivalent to 64 kg/m$^2$/h overall). The pressure used was only 0.1 MPa. Doubling the pressure (Run 42) increased the rate by 1.5 times. It can be assumed that at 0.8 MPa (120 psi), the rate would increase by a factor of $(1.5)^3$, i.e., to 216 kg/m$^2$/h overall. Increasing the temperature could increase this further. However, as indicated earlier, over 200 kg/m$^2$/h is a very acceptable rate.

It should be noted that Run 9a-LA, which was made at a solvent-to-dry-coal ratio of 1.5:1, gave a filtration rate of 93 kg/m$^2$ in 30 min at 0.34 MPa in test NCF 43. At 0.8 MPa and 300 °C, an overall rate close to 200 kg/m$^2$/h would be expected. This is the same value as deduced above by extrapolating the data from filtration of Run 8c-LA products.

## OVERALL YIELDS OF SOLIDS-FREE HIGH BOILING MATERIAL

Feedstocks for catalytic upgrading were prepared by vacuum distillation of filtrates. The yields of 566 °C$^+$ (1050 °F$^+$) material in the distilled samples seemed quite low considering the high coal conversions that were being achieved in the first stage. Table 37 shows the overall yields of both 482 °C$^+$ (900 °F$^+$) and 566 °C$^+$ (1050 °F$^+$) distillation cuts for soluble products. The data

presented are subject to some variability as a shift of 1% or 2% in the simulated distillation analysis can effect a 2% to 4% change in the yields on a dry coal basis.

The two bituminous coal runs show virtually the same yields (ca. 73%) of 482 °C$^+$ and 566 °C$^+$ fraction. This implies that there is little, if any, material produced boiling between these two temperatures. If the THFI, which represents about 12% on dry coal (6% ash, 6% IOM) are added to the high-boiling fraction, then the total product yield of heavy material (482 °C$^+$ and probably 566 °C$^+$) is 85% on dry coal. This implies that in the first stage, 15% of the coal has converted to gas and distillate boiling below 482 °C.

Several of the tests made with the undecanted material from Run 8c-LA with different amounts of distillate solvent (which contained a small amount of 566 °C$^+$ and a large fraction of 482 °C$^+$) gave remarkably similar net yields. Again, there was little indication of the production of any material between 482 and 566 °C. The other part of the Run 8c-LA product, the lighter decanted liquid, contained 6% 566 °C$^+$ material and (5% ±5% on dry coal) between 482 °C and 566 °C.

The yield of soluble material from Run 9a-LA is slightly lower. The run, however, has not been duplicated. Overall, it is concluded that for the Glenharold Mine lignite, the yield of 482 °C$^+$ material is around 50% of dry coal, of which nearly all (90%) is above 566 °C. Addition of the THF insolubles (~17% on dry coal) gives a total heavy material yield of 67% indicating a much higher yield of gas and distillate (-482°C) in the first stage.

Although full data are not available, the Black Thunder Mine subbituminous coal appears to behave similarly to the lignite.

There is 50 % more heavy extract from bituminous coal than lignite (on a dryash-free basis). Thus, it is concluded that there is more conversion to distillate in the first stage for the lower rank coals and the amount of coal extract that has to be converted to light distillate in the upgrading stage for the low-rank coals is proportionality less than for bituminous coal.

## CATALYTIC UPGRADING

## CATALYST SELECTION AND SULFIDING

### Catalyst Precursors

### Catalyst Presulfiding - Literature Review

#### Presulfiding supported Ni/Mo catalyst

One approach to evaluating the activation of Mo precursors is to compare commercially available supported catalyst properties with the properties of other candidate precursors. AKZO AO-60 (a Ni/Mo catalyst supported on alumina) was chosen for baseline use. A sample was provided by Hydrocarbon Technologies, Inc. (HTI). Information on the catalyst also was provided by HTI (Table 39). In-house determinations of Mo and Ni content were 11.3 and 2.7 wt % respectively (dry basis). This catalyst was delivered in its oxidic form, and a suitable sulfiding procedure was required. Most sulfiding operations, described for both laboratory and commercial practice, are performed under a flowing $H_2S/H_2$ mixture, usually in the range of 5-15% (commercial practice typically in the 8-12% range). However, to produce the small quantity of sulfided material needed, preparation was done batchwise in microautoclaves. Sulfiding conditions were selected based on a review of the relevant literature.

The rates of sulfiding the oxidic forms of Ni and Mo in $H_2/H_2S$ for commercial preparation of Ni/Mo catalysts on alumina are very rapid.[31] Heats of reaction are large (-30 to -40 kcal/mol). The stoichiometry is:

$$3\ NiO + H_2 + 2\ H_2S \rightarrow Ni_3S_2 + 3\ H_2O$$

$$MoO_3 + H_2 + 2\ H_2S \rightarrow MoS_2 + 3\ H_2O$$

Commercial practice is to provide about 0.11 lb sulfur per lb of catalyst to ensure ample sulfiding.

Yang et al.[32] described the effect of several presulfiding/postsulfiding techniques on a variety of Mo-containing catalysts sulfided under $H_2S$ in $H_2$. The reported S/Mo atomic ratios ranged from 1.0 to 2.4. De Beer et al.[33] reported that presulfiding at 400 °C for 2 hr in 14% $H_2S/H_2$ at one atm resulted in an S/Mo ratio of 2.04. Following essentially the same procedure, but with a one-hour postsulfidation $N_2$ purge, Massoth[34] reported a S/Mo ratio in the range of 1.6 to 1.7. His work clearly illustrated very rapid sulfidation of $MoO_3$ on alumina, which leveled off in about two hours.

Ahmed and Crynes[35] presulfided 8/10 mesh commercial Co/Mo catalysts using less severe sulfiding conditions of 232 °C for 90 min with a 5% $H_2S$ in $H_2$ mixture. It was observed that the catalyst's HDS activity gradually increased while treating a sulfur-bearing raw anthracene oil feedstock. It was concluded that although active, the catalyst probably was not properly sulfided. Hallie[36] concluded that 5% was too low a concentration of $H_2S$ mixture was too low to properly sulfide a commercial CoMo catalyst at 200 °C (for 48 hr); however, activity was much improved when presulfiding was completed at 360 °C.

Based on the information found in the literature, it appears that with ample $H_2S$ present, considerable sulfidation can be expected within about one hour, and near equilibrium sulfur addition can be expected over the course of two hours in an $H_2S/H_2$ atmosphere at 400 °C. The sulfur addition expected would be in the range of 1.6 to 2.0 S/Mo atomic ratio. The extent of sulfidation at lower temperatures could be incomplete.

### Catalyst Presulfiding - Catalyst Selection

In order to ascertain the need to presulfide the catalysts to attain high activity, and to aid in selecting the most effective dispersed catalyst precursor, a series of upgrading experiments was conducted in microautoclaves at 440 °C for 60 min under 2% $H_2S/H_2$ using Wilsonville Run-258A deashed resid as the feedstock. Three catalyst precursors were evaluated: two dispersed organometallics (Molyvan L and Mo naphthenate) and a supported Ni/Mo catalyst on alumina (AKZO AO-60). A sample of the AO-60 sulfided *ex situ* also was prepared for activity comparison. Each of the catalysts was tested in a single run. Catalysts that were sulfided in situ were subsequently tested with a thermal pretreatment step at 375°C for 30 min. The results are presented in Table 40.

Each of the Mo precursors improved resid conversion over that found (19%) without added catalyst. Conversions with catalyst were 35-38%, either with or without pretreatment. The one exception was the AO-60 catalyst that had been thermally pretreated. AO-60 either benefited from pretreatment or, alternatively, exhibited some activity during the 30 min pretreatment period to increase resid conversion to an average of 45% (average of two determinations). The AO-60 catalyst presulfided ex situ exhibited the next highest activity. A scale of resid conversions was established (no catalyst addition to that obtained by presulfiding the commercial AKZO AO-60 catalysts). Performance of the dispersed catalysts was referenced to this scale. Each dispersed

catalyst exhibited good activity, comparable to the activity when a presulfided supported catalyst was present at the same concentration levels.

Based on a comparison of 566 °C$^+$ resid conversion and hydrogen consumption, Molyvan L was selected to further evaluate the need for presulfiding. The Molyvan L was chosen because it exhibited activity within the first few minutes of reaction, based on total pressure data. It is a commercial product; therefore, better characterization, quality control, and wide product availability are anticipated. Importantly, the Molyvan L has successfully been used in coal liquefaction research, including large-scale coal liquefaction processes.

## Elemental Balances

Six of the catalytic upgrading experiments designed for catalyst activity screening also provided elemental balance data. The results are presented in Table 41. The resid and distillate yields were determined by weight of recovered material. Balances for C and H average ca. 98%, and that for S average ca. 93%. These values provide confidence in the experimental methods used for catalytic upgrading tests.

## Fate of Molyvan L Detritus

An investigation was made to determine the fate of the Molyvan L organic component. At 1000 ppmw Mo, the total weight of material used is ~0.03 g. To account for this contribution to the organic content of the reaction system, the equivalent amount of $MoS_2$ is assumed to report to and is subtracted from the resid weight; the remainder is assumed to report to the distillate fraction and, therefore, does not enter into the resid conversion calculation. At 1% Mo, the organic component of the catalyst precursor may affect the apparent conversion rate of the resid feedstock if it reports to the residual fraction. Accordingly, an upgrading experiment was conducted with a 20% Molyvan L/80% Wilsonville Run 258A heavy distillate mixture at 440°C for 60 min under 2% $H_2S$ in $H_2$ gas mixture. The products of reaction were recovered with THF and analyzed by Simulated Distillation (SIMDIS). The boiling curve generated was compared with a SIMDIS of the same mixture of materials prior to reaction to determine if any weight was added in the 566 °C$^+$ boiling range material (5.0% in the starting heavy distillate). Correcting for the amount of $MoS_2$ that should be present at the end of the reaction, the 566 °C$^+$ fraction was calculated to be only 2.9%; no net materials were added to the resid fraction. This 2.9% represents a maximum impact at very high Mo loadings. Assuming this amount had been added

to the resid fraction in a typical experiment, the maximum increase in resid conversion is +1.2%. Accordingly, no adjustment was made in subsequent tests for the Molyvan L organic component.

## CATALYST PRETREATMENT

To ensure that the molybdenum in the Molyvan L could convert to the active sulfide form, a series of pretreating experiments was conducted. Wilsonville Run 258A DAR and Molyvan L were pretreated at selected times and temperatures, followed by catalytic upgrading reaction. All tests used 2% $H_2S$ in hydrogen to sulfide the Mo; pretreatment time (0, 5 and 30 min), pretreatment temperature (300, 340, 375 and 440 °C) and residence time (30 and 60 min) were varied. Pretreatment was accomplished by agitating the reactor at the surface of a heated, fluidized sand bath. At the end of the pretreatment period, the reactor was fully immersed in the fluidized sandbath for the catalytic upgrading reaction. Data are summarized in Tables 42 and 43, and in Figures 37 through 39. In comparison to runs where no catalyst was added, as well as in runs in which a supported Ni/Mo catalyst presulfided ex situ was used, it appears that the Molyvan L was able to participate in the reaction within the first few minutes of the experiment. Furthermore, over the range of conditions tested, pretreatment had little effect on Molyvan L catalyst activity, as determined by its use in subsequent catalytic upgrading tests.

A plot of reaction time in minutes vs. log resid remaining for three pairs of duplicate experiments is shown in Figure 40. The reaction is fairly well represented by first order kinetics, with respect to the disappearance of resid, for the first 60 min. The reaction eventually slows in the 60 to 90 min period, when only the more refractory resid remains. There is no indication that a more active Mo catalyst form was generated in pretreatment. These data indicate that an active form of the catalyst was present at the beginning of the experiment, and it remained active throughout. Based on the results of the experimental work, it was determined that pretreatment of the catalyst over the times and temperatures tested was not required for good, reproducible catalyst effect.

## CATALYTIC UPGRADING OF FIRST-STAGE PRODUCTS

A series of eight experiments was conducted using both the first-stage product filtrate and Wilsonville Run 258A deashed resid (DAR). First-stage product filtrate was available from several microautoclave runs that had been filtered under four sets of conditions. These filtrates were combined to make one master sample. The resid content was increased to 72% 566°C$^+$ by distillation. Sixty-minute reactions were conducted at two temperatures (400 and 440 °C),

and at two catalyst loadings (1000 and 10,000 ppmw Mo introduced in Molyvan L) under 2 wt % $H_2S$ in $H_2$ using Molyvan L as the catalyst precursor. The results are summarized in Tables 44 and 45. Resid conversions at 440 °C for the first-stage product filtrates were higher than for the DAR. At 400 °C, conversions appeared to be comparable.

Changes in resid conversion as a function of resid concentration were explored. An equal amount of Wilsonville Run 262E V1074 heavy distillate, 488 °C⁻ (910 °F⁻) fraction, was added to dilute the resid content of the filtrates. Those results are summarized in Table 46. Catalytic upgrading experiments also were conducted at intermediate severity (420 °C). Although not linear across the entire range, curvature in key results at the intermediate conditions was small. A linear model designed to cover this range would be useful in determining an integrated process design.

## COAL RANK

Table 47 focuses on several key hydrotreating parameters, with the emphasis on the impact of coal rank. Each of the experiments shown was conducted at 440 °C for 60 min, using 1% Mo in Molyvan L. .

The filtrates prepared from subbituminous coal are least efficient with respect to $C_1$-$C_3$ gas yield and hydrogen consumed per gram of resid converted, and generally have low resid conversions. The lignite-derived filtrates have higher resid conversions, with medium efficiency at the same hydrotreating conditions. The one experiment made with bituminous coal-derived filtrate is comparable to the lignite with respect to $C_1$-$C_3$ gas yield and hydrogen consumed per gram of resid converted, but resid conversion is lower.

Resid conversions for all first-stage product filtrates is much higher than that which was obtained with the DAR. Gas make per unit resid conversion was comparable. Hydrogen utilization with the first-stage product filtrates was better. The one test in which distillate-diluted DAR was fed, R6-19-1, shows better hydrogen utilization, but the calculated hydrogen consumption is quite small and experimental error could easily be ± 30% of that value.

High resid conversion in the upgrading of the product of one-liter autoclave test Run 9-LA with its high resid content argues in favor of reducing the amount of vehicle solvent fed to the hydrotreater. Resid conversion is high, and the efficiency numbers are good.

## PARAMETRIC STUDY ON FILTERED FIRST-STAGE PRODUCTS

A $2^3$ factorial experiment was planned to better understand the characteristics and behavior of the first-stage liquefaction products, Preliminary data from scoping studies made at 400 and 440 °C and with Mo concentrations of 1000 and 10,000 ppm formed the basis for the experimental plan. Using the results of the parametric study, a simple linear model was developed. Optimum conditions were selected for hydrotreatment, at minimum $C_1$-$C_3$ gas yield. Three factors were selected for evaluation in the study (Table 48).

The combined product of one-liter autoclave test Runs 8a-LA and 8b-LA, which were prepared from Glenharold Mine lignite at 350 °C , 60 min, was filtered and distilled to produce a master sample of about 60 g. This sample was subsequently divided into six aliquots. The filtrate sample was distilled and found to contain 38.3% 566°$C^+$ resid. The as-received filtrate also was analyzed by SIMDIS and found to contain 40.0% resid.

Experiments were run in duplicate, using 2 grams of feedstock and Molyvan L (either as received or diluted 1:1 with hexadecane) as the catalyst precursor. The reactor was charged to a total cold pressure of 10.1 MPa with hydrogen, and contained 2% $H_2S$ to provide ample sulfur to convert the Mo to its sulfided form. Earlier experiments had shown $H_2S$ present in the product off-gases, and most experiments here gave $H_2S$ concentrations in the 2-3% range. Based on the outcome of the presulfiding study, it had been decided that reactions would be conducted without any pretreatment.

Six effects were analyzed using a statistical program designed for two-level factorial experiments. Linear mathematical models were developed for each of those effects, selecting coefficients from one-way (main), two-way and three-way interactions and retaining only those that showed a high level of statistical significance. Most of the common models contained only the main effects, with no two- or three-way interactions. Table 49 reports the correlation coefficients for the models found to be the best fit for the data, and Table 50 shows the parameters, in coded format, for each of the six linear models. The coded coefficients may be translated to "real variable" units by dividing the coded coefficient by one-half of the difference between the high and low values studied for the particular coded factor represented. For example, the decoded form of the resid conversion model is:

$$\% \text{ Rc} = 48.41 + .524(\text{time, min} - 45) + .686(\text{Temp,}^{o}\text{C} - 420) + 4.958 \text{ x } 10^{-4}(\text{Mo conc, ppm} - 5500)$$

Shown in parentheses in Table 50 are the probability (P) values for the coefficients. These values represent the probability that a particular coefficient is zero. If not shown, the coefficient is assigned a zero value). Most P values for the selected coefficients are quite low.

Response surfaces were generated for resid conversion (Figure 41), $C_1$-$C_3$ gas yield (Figure 42), and hydrogen consumption (Figure 43). To visualize these responses in three dimensions, the concentration of Mo was held constant while time and temperature were varied across their ranges. Since the graphs were all generated with Mo at its lowest level (1000 ppmw), the corresponding value at its highest level can be calculated by adding twice the Mo coefficient shown in Table 50. For example, for the resid conversion response at 10,000 ppm Mo, add:

$$2 \; x \; 2.23 \; = \; 4.46$$

to each value shown in Figure 41. Since the models each show the Mo coefficient as a positive value, higher Mo loadings always give higher responses.

Note that any calculated effects away from the "corners" of these surfaces do not recognize any curvature that may be present. More experiments would be required for a detailed response at the midpoints of the selected ranges.

Figure 44 shows both $C_1$-$C_3$ gas yield and hydrogen consumption as a function of resid conversion. This graph was generated by selecting two hundred random times and temperatures and calculating the effects using the linear models that were developed. Again, Mo concentration was held constant at the 1000 ppm level. Significant differences in gas make become apparent at >40% resid conversion. A separate plot using a fixed temperature and Mo concentration shows the low gas makes are associated with experiments at 400°C. Run time is a significant positive coefficient in the resid conversion model, and longer run times give higher conversions.

In Table 51, the product yield data developed in the parametric study are tabulated. Table 52 contains C, H, and N data for the as-received (AR) feedstock (NCF28..32), its 566°C⁻ distillate

fraction (R6-204-1D) and the 566 °C$^+$ fraction (R6-204-1R). The nitrogen value for the as-received feedstock was calculated from analyses of the resid and distillate portions of the feedstock.

Analyses of distillate and residual fractions of hydrotreated products also are presented in Table 52. Because of the small sample size obtained from the microdistillation, in a number of cases there was insufficient sample to obtain an elemental analyses. In all cases, sample size was limited to obtaining carbon, hydrogen, and nitrogen analyses only. Thus, sulfur, oxygen, and ash are provided as a lumped difference value. In the distillation, water and light hydrocarbons are lost. This can explain why, in several cases, the hydrogen content of the distillate fraction is lower than the hydrogen content of the distillate fraction ofthe as-received feedstock. The ash content of the feedstock was 0.07 wt %. Thus, the ash contents of the hydrotreated products are expected also to be low. High values for the difference value of S+O+ash can be attributed to the introduction of sulfided catalyst (and sulfiding agents). Figure 45 shows the simulated distillation results for each of the parametric study products. Two SIMDIS analyses are shown on each graph, one for the 566 °C$^+$ resid and one for the corresponding distillate. Those data are composited on the figure to show the percent mass relationship between gas yield, distillate and resid that was calculated for the experiment.

## SIMULATED RECYCLE

In order to obtain an estimate of the activity of the dispersed catalyst after reaction, and of its utility for recycle with unconverted resid, an experiment was conducted using the Wilsonville deashed resid (DAR). Single-pass reaction conditions were 440 °C for 60 min. An experiment was performed (R6-134-1 and 2) where Molyvan L, sufficient to give 1000 ppm Mo overall, was added to only 10% of the DAR charge. This mixture was reacted at 440 °C for 60 min to simulate the first pass. The gases were collected, the reactor opened, and the remaining 90% of the DAR was added; the second pass then was effected. Using data from an earlier experiment with 10,000 ppm Mo loading to calculate the total resid feed to the second pass, a second pass resid conversion of 33.7% was calculated. This is slightly better than the single pass resid conversion of 32% determined earlier using all fresh feedstock (in R6-51-2). Results of these experiments are reported in Table 53.

In other experiments, the DAR was reacted with Molyvan L at the 1000 ppm Mo level in a first pass. The products were distilled to an atmospheric equivalent temperature (AET) of 566 °C and

the resid recovered (R6-74-1). Fresh DAR and heavy distillate were added to return the reactor feed to 3 g for a second pass (R6-88-1) with the same 566 °C$^+$ and 566 °C$^-$ composition as in the first pass. Because of losses in recovering the resid, the concentration of Mo in the second pass was 200 ppmw lower than the first pass, but the effect on conversion due to this lower concentration is smaller than that which can be estimated from available data. Assuming there is no change in the reactivity of the recovered and distilled resid portion containing the recycled catalyst, any deviation from the earlier correlated performance could be attributed to a change in the activity of the recycled Mo. However, in this experiment, most of the resid feed is generated in the first pass, and its reduced reactivity is probably reflected in the lower 25% resid conversion. Further, the recycled resid fraction is recovered with THF and exposed to a 331 °C vacuum distillation.

Figure 46 is a plot of the total reactor pressure for these two passes, and their nearly equal pressure histories suggest that the Mo is similarly active in the second pass. A pressure profile for the same reaction without added Mo is shown for reference, and the immediate pressure reductions evident in the previous experiments is absent.

To determine the effect of fresh catalyst addition to the recycled catalyst in between the first and second pass, similar to what happens in an operating plant, 100 ppm fresh Mo was added as Molyvan L (R6-114-1). Other procedures remained the same as with the previously described experiment. Resid conversion in the second pass for this single experiment returned to the levels seen earlier. Note that for each of the recycle experiments, hydrogen consumption is reduced below that of the single pass experiment, as is hydrocarbon gas make.

Solid distillation resids from two of the hydrotreating experiments with DAR feedstock were graphite coated and subjected to SEM-EDS studies [Hitachi S-2700], in hopes of preparing concentration maps of S and Mo to determine if the two are associated and well distributed. Unfortunately, Mo electron scatter obscures that of S (ca 2.5 keV) so that if Mo is present, S is indeterminate and the question of their association is not answered. Nonetheless, in one sample with a 10,000 ppmw Mo loading, the Mo was found to be well dispersed across the sample, with occasional "hot spots". In the second sample with only 1000 ppmw Mo on feed, the signature Mo signal (ca 17.5 keV) was below the detection limit of the instrument. The common S/Mo peak was also found to be well distributed across the sample.

Based on the evidence of this work, we concluded that recycled Mo prepared from fresh Molyvan L, sulfided in the presence of a coal liquefaction resid, would initially exhibit activity in recycle comparable to its activity in the first pass. Further study is required to determine catalyst behavior in subsequent recycle/processing.

# CONCLUSIONS AND PLANS

## PROGRAM

### CONCLUSIONS

Technical aspects of the novel concept coal liquefaction program were successfully demonstrated in Task 2. High coal conversions were obtained under low-severity conditions. The products of dissolution are readily filtered for removal of insoluble materials and the filtrates are readily upgraded with dispersed catalyst. Coal conversions were maintained in scaling the reactions from 45 mL microautoclave-scale to one-liter autoclave-scale. The literature search of hydride ion-donation reagent synthesis was completed. The preliminary technoeconomic evaluation made in Task 2 indicates that the process can produce significantly higher distillate product at lower hydrocarbon gas make than conventional liquefaction technologies. The cost of hydride ion-donation reagent generation was identified as a major component of the overall process costs.

### PLANS

Task 3 studies will include continued investigations with alternative hydride ion sources. Consideration will be given to alternative hydride ion sources or combinations of sources which promote high coal conversions at low-severity conditions and which present an economic advantage. Obtaining good material balances around the first stage (especially obtaining information on hydride ion reagent recovery) was identified as an important goal for Task 3.

In Task 3, the first-stage hydride-ion-promoted solubilization step will be integrated with the filtration step. This will eliminate reheating the first-stage product prior to filtration. A realistic first stage environment presumably would have present a mixture of first- and second-stage solvents and the solubilized first-stage products. A first-stage solvent with appropriate properties to model this combined solvent system will be produced and a study using it will be undertaken in Task 3.

To confirm the higher reactivity of products produced with hydride ion promoted liquefaction, as compared to the Wilsonville deashed resid, tests are planned to produce single-pass products using "conventional" liquefaction conditions. The tests will be made in the one-liter autoclave and products will be subjected to filtration and second-stage catalytic upgrading.

A large-scale catalytic upgrading reactor will be designed, built, and tested with filtered first-stage products in Task 3. Studies for choice of optimal second-stage catalyst will be continued under Task 3. Resid recycle tests will be made in the large-scale reactor in an effort to achieve 90% overall conversion.

The preliminary conceptual plant design developed in Task 2 will be refined as additional experimental data are generated in Task 3.

Plans for Task 4 are to move the project toward integrated testing. The conceptual flow sheet developed under Task 3 will be used to guide the experimental testing either in a blocked out or partially integrated manner. The results of testing under Task 4 will be the basis for a final engineering and economic evaluation and for recommendations concerning further development of this novel concept toward an integrated continuous bench-scale unit.

## SOLUBILIZATION AND PRODUCT CHARACTERIZATION

### CONCLUSIONS

In Task 2:

- High coal conversions of greater than 90 wt % have been achieved with coals of three different ranks.
- High coal conversions are obtainable at 350-400 °C.
- High coal conversions indicate that the occurrence of retrograde or secondary reaction to intractable, insoluble materials is minimized at these low temperatures.
- Coal conversions obtained with hydride ion reagents are higher than those obtained with molar equivalents of CO or CO/methanol.
- Maximum coal conversions are achieved at short-to-moderate residence times (30 to 60 min).
- The reaction system operates at moderate autogenic pressure (1000-4000 psi).
- Solvent is necessary to achieve high coal conversions, but a hydrogen-donating solvent is not required.
- The aromatic content of the solvent is important for high coal conversions at the lowest severity reaction conditions.
- Reaction products are enriched in hydrogen and depleted in oxygen relative to the feed coal.

- First-stage products are easily filtered with a constant pressure filter (see Filtration, below).
- The distilled, filtered, first-stage products are upgradable with dispersed catalyst (see Catalytic Upgrading, below).
- One-liter autoclave tests were successfully executed using two methods of product recovery.

### PLANS

In Task 3, the focus will be on integration of the first-stage and filter operations. A flash of light first-stage products will be incorporated into the product collection schemes. The bottoms will be filtered. First-stage solvents will be tested to simulate a realistic plant environment and to aid in efficient filtration operation. Subbituminous coal will continue to be tested as an alternative feed. Microautoclave testing with a variety of hydride-ion sources will continue at low-severity conditions.

## FILTRATION

### CONCLUSIONS

Hot pressure filtration was demonstrated as an effective method for the removal of solids from the first-stage products. The rates of filtration achieved at around 300 °C and 0.3 MPa with the feedstocks made from several coals (bituminous, subbituminous and lignite) indicate that the filtration in a commercial plant would contribute only about 40¢/bbl of oil in processing cost (i.e., capital and running costs).

The solids were shown to be capable of bridging across relatively large orifices (e.g., 100 µm x 500 µm). This would enable a coarse and relatively robust material to be used as the filter screen. When tested, the quality of filtration achieved with such a screen was not distinguishable from that obtained with a 1 µm (nominal) glass fiber paper.

The optimum distillate solvent-to-coal ratio for filtration is around 1:1 or 1.5:1 depending somewhat on the coal, the extraction conditions (severity) and the filtration temperature.

The viscosity determinations on filtrates and filtrates concentrated by vacuum distillation indicate that the majority, but definitely not all of the diluent could be recovered before upgrading and still give a pumpable fluid at 300 °C. Total decoupling of the extraction and upgrading stages would

not be practical on a large scale as neat coal extract, or the separated 566 °C$^+$ (1050 °F$^+$) fraction, do not soften until around 300°C.

At solvent/diluent-to-coal ratios of 1:1 or 1.5:1, washing the filter cake to recover extract for these coals is not economic. About 2% of the coal (other than ash and IOM) is discarded with the filter cake by omitting a wash stage in the filtration cycle. This would effectively lower first-stage conversion from 92% to 90%. This is a small amount compared with the reduction in conversion of 5 to 20% obtained with other solid-liquid separation methods, such as critical solvent deashing (ROSE-SR) and vacuum distillation processes.

### PLANS

A Filter assembly will be designed and constructed that is large enough to accept the entire first-stage one-liter autoclave charge (ca. 300 mL). The filter will be designed for an operating temperature of 300 °C, pressure differential up to at least 0.8 MPa (120 psi), and maximum operating pressure of 3 MPa. The filter element will be a Conidur (100 µm x 500 µm) screen.

Initial tests will provide information on the effect of cooling reactor products to room temperature and reheating for filtration. Several such runs will be performed, and the products will be upgraded. After filtration, the filter will be evacuated in order to recover distillate which will form part of the potential recycle distillate solvent. The filtrate will be concentrated by vacuum distillation, either in situ from the filtrate receiver vessel or in separate apparatus. This will produce a feedstock for second-stage catalytic upgrading and more distillate solvent for recycle. Various potential first-stage solvents/filtration and recycle distillate solvents will first be tested.

## CATALYTIC UPGRADING

### CONCLUSIONS

Among the Mo precursors tested, satisfactory hydrotreating results were obtained with the selected dispersed catalyst, Molyvan L. Using a surrogate deashed resid from Wilsonville (DAR) in comparison hydrotreating screening experiments, conversions of 566 °C$^+$ resid with the Molyvan L were comparable to conversions with Mo naphthenate, with and without pretreatment, and with a presulfided, supported Ni/Mo catalyst. However, the supported Ni/Mo catalysts with a 30 minute, 375 °C pretreatment gave higher conversion. Total pressure records of hydrotreating experiments indicated that Molyvan L is active within the first minutes of reaction.

Pretreatment to convert the Mo to the active sulfide species is not required in runs of 30 min and longer.

Using Molyvan L in further studies, an operating region of improved hydrogen utilization, yielding less hydrocarbon gas for a given resid conversion, was identified from a parametric study evaluating reaction time, reaction temperature and catalyst loading. Analysis of the catalyst concentration data showed little incentive to process the filtrate with Mo concentrations in the range above 1000 ppmw, since the observed effect could be producedmore economically by changing either reaction time or temperature. Separately, a hydrotreating experiment feeding a more concentrated resid (less vehicle solvent) was found to give high resid conversion, with good efficiency, arguing in favor of minimizing vehicle solvent feed to the hydrotreater.

Recycled Mo prepared from fresh Molyvan L, which was sulfided in the presence of a coal liquefaction resid, initially exhibited activity in recycle comparable to its activity in the first pass.

Based on the work presented here, it was observed that the hydride prepared filtrates tested were more reactive than the coal derived deashed resid from Wilsonville which was selected for comparison. At the most severe conditions tested (440 °C for 60 min with 10,000 ppm Mo), 566 °C$^+$ resid conversion averaged 72%, with 27 mg/g (MAF feed basis) hydrogen added for a filtrate prepared from Glenharold lignite. At the same conditions using the DAR as feedstock, resid conversion averaged only 31%, even though hydrogen uptake averaged 32 mg/g.

## PLANS

There are four key objectives for this portion of Task 3, to be performed at UK/CAER, investigating the hydrocracking characteristics of materials produced by CONSOL:

1. To scale the design of the catalytic upgrading stage to match that of the integrated first-stage and solids separation units.

2. To provide more detailed simulated recycle experiments, as well as other process material balance information on the dispersed catalysts (or similarly, reliable information on the relative aging of supported catalysts, should they be employed further).

3. To conduct recycle experiments to achieve a targeted goal of 90% overall conversion.

4. To generate hydrotreated products in sufficient quantity to be evaluated by CONSOL as a vehicle solvent for the first stage, if called for by the revised conceptual design.

It is likely that work will continue with both supported and dispersed catalysts, performed in both the larger CSTR and microautoclaves where required. To that end, work is presently underway to adapt an existing 300 mL CSTR at the CAER for continuous high pressure (17.3 MPa or 2500 psig) hydrogen flow. The equipment has only been used in batch mode to date, and calculations showed that the hydrogen available in the headspace above a 100 g feed charge would not be sufficient for the upgrading operations planned. Both upstream gas control, sulfur addition equipment, and downstream measurement and separation facilities will be added. In the scaled-up equipment, liquid and solid feedstocks and catalyst precursors will be added batch-wise. The catalyst precursors will be sulfided by dimethyl disulfide (DMDS), which will be added to the flowing hydrogen feed gas by vapor saturation in a temperature-controlled DMDS charge vessel.

Dispersed soluble catalyst precursors can be added directly to batch feed mixture, and when supported catalyst are to be tested, they will be added directly in powdered form as well.

## ENGINEERING AND ECONOMIC EVALUATION

### CONCLUSIONS

Results of the technical evaluation to date appear to indicate that a novel concept-based liquefaction plant for Glenharold Mine lignite can produce a significantly higher distillate product yield at a lower light hydrocarbon gas make than conventional liquefaction technologies which have been tested at the pilot plant scale of operation. This conclusion is preliminary, since much of the data upon which the novel concept integrated liquefaction system balance has been based is estimated. Experimental data generated during the upcoming Task 3 work will enable a more definitive conclusion to be made.

Using published cost data, a preliminary estimate of the cost of hydride ion reagent "A" was made. Capital and operating costs were estimated for a plant producing hydride ion reagent "A" in the quantities that might be required in a full-scale commercial liquefaction plant. It was estimated that cost of producing very large quantities of hydride ion reagent "A", exclusive of feedstock costs, would be approximately $.05/lb. If the consumption of hydride ion reagent "A" was 0.5 lb/lb of MF coal fed to liquefaction, the cost of using hydride ion reagent "A", exclusive of feedstock costs, is estimated to be approximately $15 per barrel of product. Therefore, the

use of hydride ion reagent "A" would appear to have a significant effect on the economics of the process.

To reduce the cost of reagent regeneration, exploratory research must be done to investigate the use of low concentrations of hydride ion donation reagents in the first stage solubilization reaction. This could possibly be done by combining the reagents with other active, but less expensive, coal solubilizing agents such as carbon monoxide and methanol.

A novel concept liquefaction case was developed based on the experimental work with Glenharold lignite. The elementally balanced liquefaction yield structure was determined based on one liter Run 8-LA, filtration tests, and the catalytic upgrading parametric study of the filtered Glenharold extract. The preliminary yields indicate a $C_4^+$ distillate yield in excess of 60 wt % on MAF coal at a light hydrocarbon gas yield of approximately 6%. These yields are superior in both respects to the yields obtained with similar coal feeds at the Wilsonville liquefaction pilot plant (Run 255, Texas lignite) and Australian brown coal liquefaction pilot plant. The above results indicate the potential merit of the hydride-ion concept. Complete data on the novel concept liquefaction case are given in Confidential Appendix III.

## PLANS

A technical and economic evaluation of the novel concept case for Glenharold Mine lignite will be completed. Balances for the C4+ distillate upgrading step to gasoline will be estimated, gasification system balances and requirements will be defined, and the balances for makeup hydrogen, makeup carbon monoxide and fuel gas will be closed. The economic evaluation will include the estimation of capital and operating costs for the conceptual commercial plant leading to the estimation of a required gasoline product selling price. During the economic evaluation, key cost areas will be identified and suggestions for improving the economics of the process will be fed back into the plans for the experimental work.

Review and analysis of the experimental data generated during Task 3 will be made as the information becomes available. Updates to the conceptual commercial plant design for the novel concept case will be made based on this updated information.

Work on the selection of a baseline case will continue. Data from Wilsonville Run 255 will be thoroughly reviewed to determine if the available information is sufficient for the development of

the baseline case. Once an affirmative determination is made, the technical and economic evaluation of a conceptual commercial liquefaction plant based on this run will begin.

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TABLE 1

ANALYSES OF COALS USED IN TASK 2

| Ultimate, wt% Dry | Freedom Mine Lignite - LA[a] | Freedom Mine Lignite - HA[b] | Glenharold Mine Lignite | Black Thunder Mine Subbituminous | Ohio 11 Mine Bituminous |
|---|---|---|---|---|---|
| C | 68.66 | 63.21 | 63.06 | 70.32 | 75.45 |
| H | 4.33 | 3.91 | 4.44 | 4.68 | 5.17 |
| N | 0.90 | 0.81 | 0.94 | 1.04 | 1.53 |
| Cl | 0.038 | 0.037 | 0.031 | 0.035 | 0.099 |
| S | 0.55 | 0.97 | 1.33 | 0.50 | 3.09 |
| O (by diff) | 21.06 | 19.64 | 20.72 | 17.89 | 7.95 |
| $SO_3$-free Ash | 4.46 | 11.42 | 9.48 | 5.54 | 6.71 |
| Major Ash Elementals, wt% | | | | | |
| $SiO_2$ | 12.89 | 35.33 | 31.80 | 31.48 | 43.36 |
| $Al_2O_3$ | 10.13 | 14.30 | 12.42 | 15.76 | 18.74 |
| $TiO_2$ | 0.39 | 0.52 | 0.49 | 1.14 | 1.04 |
| $Fe_2O_3$ | 6.14 | 6.59 | 7.09 | 5.48 | 25.80 |
| CaO | 32.55 | 12.46 | 14.07 | 21.34 | 3.83 |
| MgO | 10.08 | 5.26 | 4.05 | 4.30 | 0.79 |
| $Na_2O$ | 2.77 | 8.78 | 6.02 | 0.48 | 0.74 |
| $K_2O$ | 0.29 | 1.72 | 1.14 | 0.49 | 2.17 |
| $P_2O_5$ | 0.55 | 0.29 | 0.15 | 0.96 | 0.15 |
| $SO_3$ | 23.03 | 15.61 | 21.16 | 17.26 | 2.11 |
| UND | 1.18 | -0.86 | 1.61 | 1.31 | 1.27 |
| Moisture, % | 20.69 | 11.93 | 10.82 | 22.40 | 3.05 |
| Btu/lb, dry basis | 11203 | 10498 | 10649 | 11978 | 13424 |
| MAF Btu/lb, dry basis | 11892 | 12141 | 12105 | 12837 | 14444 |

a. LA = low ash  b. HA = high ash

## TABLE 2. ANALYSES OF SOLVENTS USED IN TASK 2

| Ultimate, wt % MAF | Wilsonville Run 262 Period E, V1074 Recycle Solvent, 488°C⁻ distillation fraction | Wilsonville Run 262 Period E, V1074 Recycle Solvent | Lummus Pilot Plant Run 3LCF7, Pasting Solvent Distillate | Reilly Industries Anthracene Oil | Kawasaki Anthracene Oil |
|---|---|---|---|---|---|
| C | 89.25 | 88.86 | 89.84 | 91.36 | 90.04 |
| H | 10.65 | 9.91 | 8.65 | 5.74 | 6.21 |
| N | 0.28 | 0.44 | 0.30 | 0.97 | 0.81 |
| S | 0.03 | <0.03 | 0.24 | 0.55 | 0.87 |
| O (by diff) | -0.23 | 0.79 | 0.97 | 1.38 | 2.07 |

## TABLE 3. TASK 2 SOLVENT ANALYSES PROTON DISTRIBUTION(a)

| Solvent (b) | Proton Distribution, % | | | | | | |
|---|---|---|---|---|---|---|---|
| | Cond Arom | Uncond Arom | Cyclic Alpha | Alkyl Alpha | Cyclic Beta | Alkyl Beta | Gamma |
| WD | 8.9 | 4.7 | 12.6 | 7.6 | 14.7 | 36.2 | 15.3 |
| WW | 11.1 | 3.9 | 13.9 | 7.4 | 15.3 | 34.9 | 13.6 |
| L | 18.5 | 8.3 | 13.2 | 9.0 | 19.6 | 19.6 | 11.7 |
| K-AO | 77.6 | | 19.6 | | 2.2 | | 0.6 |
| R-AO | 85.5 | | 12.5 | | 2.0 | | 0.0 |

a. Determined by $^{1}$H-NMR Spectroscopy.

b. WD = Wilsonville Run 262E V-1074, distillate
Run 8-LA = recovered solvent from one-liter autoclave test Run 8-LA
WW = Wilsonville Run 262E V-1074
L = Lummus Run 3LCF7 pasting solvent
K-AO = Kawasaki anthracene oil
R-AO = Reilly Industries anthracene oil

TABLE 4

CALIBRATION GASES

| Component | Volume % |
|---|---|
| methane | 8.0 |
| ethane | 3.0 |
| ethylene | 0.5 |
| propane | 2.0 |
| propylene | 0.5 |
| n-butane | 1.0 |
| i-butane | 0.5 |
| 1-butene | 0.5 |
| trans-2-butene | 0.5 |
| cis-2-butene | 0.5 |
| n-pentane | 0.5 |
| i-pentane | 0.5 |
| carbon monoxide | 1.0 |
| carbon dioxide | 1.0 |
| nitrogen | 0.5 |
| argon | 1.0 |
| hydrogen | 78.5 |

TABLE 5

OPERATING CONDITIONS OF HIGH-TEMPERATURE
SIMULATED DISTILLATION APPARATUS

| | |
|---|---|
| Sample Concentration | 1 wt % |
| Solvent | $CS_2$ |
| Injected Volume | 1 µL |
| Inlet Type | AC PTV, direct injection |
| Inlet Temperature, initial | 100 °C |
| GC oven temperature, initial | 40 °C |
| Detector temperature, isothermal | 430 °C |
| Inlet temperature, final | 430 °C |
| GC oven temperature, final | 430 °C |
| Oven program rate, linear | 10 °C/ minute |
| Final hold time | 3 minutes |
| Data System | HP Chemstation |
| Data Sample Rate | 5.0 Hz |
| Column | 5 m, 0.53 mm ID, 0.09 µm methyl silicone |
| Carrier | He, 20 mL/minute, constant flow |

TABLE 6

ULTIMATE ANALYSIS OF DEASHED RESID FROM ROSE-SR UNIT RUN 258A[37]

| Component | wt % |
|---|---|
| C | 90.80 |
| H | 6.86 |
| N | 1.13 |
| S | 0.06 |
| O (diff) | 1.05 |
| ash | 0.10 |
| Total | 100.00 |

TABLE 7

VARIABLES INVESTIGATED IN FIRST-STAGE SOLUBILIZATION TESTS

| Variable | |
|---|---|
| coal (coal rank) | Freedom Mine, North Dakota lignite - low sodium<br>Freedom Mine, North Dakota lignite - high sodium<br>Glenharold Mine, North Dakota lignite<br>Black Thunder Mine, Wyoming subbituminous<br>Ohio 11 Mine, Kentucky bituminous |
| residence time, min | 0, 30, 45, 60, 120, 150 |
| temperature, °C | 350, 375, 400 |
| solvent | Wilsonville Run 262E, V1074<br>Wilsonville Run 262E, V1074, 488°C⁻ distillate<br>Lummus 3LCF7 pasting solvent 454°C⁻ distillate<br>tetralin<br>Anthracene Oil - Reilly Industries<br>Anthracene Oil - Kawasaki |
| solvent/dry coal ratio, w/w | 0 - 4.4 (majority of tests made at 1.5 - 2.2) |
| hydride ion source | Hydride reagents "A", "B", and "C" |
| hydride ion reagent/dry coal ratio, w/w | 0 - 6.9 (majority of tests made at 1.0 and 1.5) |
| total water/dry coal ratio, w/w | 0.1-1.7 (majority of tests made at 0.3-0.4) |
| reactor charge, g | 9.0-35.3 |
| autogenic pressure[a], psi | 1120 - 3400 |

a. calculated

TABLE 8

## SELECTED COAL SOLUBILIZATION TESTS
## 45 mL MICROAUTOCLAVE SCALE

| Run No. | Coal (a) | Solvent (b) | Time, min | Temp, °C | HI[c]/Coal, w/w | Pressure (d), psia | Coal Conversion (e) |
|---|---|---|---|---|---|---|---|
| 11 | FM-LS | D | 45 | 400 | 1.1 | 1201 | 90.4 |
| 5 | FM-LS | D | 45 | 375 | 1.4 | 2705 | 91.0 |
| 18 | FM-LS | D | 45 | 400 | 1.4 | 2811 | 90.4 |
| 60 | FM-LS | D | 150 | 375 | 1.4 | N/A (f) | 92.4 |
| 90c | FM-HS | D | 150 | 400 | 1.1 | 2679 | 91.4 |
| 78 | GH | D | 60 | 400 | 0.9 | 1790 | 91.9 |
| 84 | GH | D | 60 | 400 | 1.1 | N/A | 91.4 |
| 94 | GH | W | 60 | 350 | 1.5 | 3312 | 92.7 |
| 94b | GH | W | 60 | 350 | 1.5 | 3312 | 92.4 |
| 96 | GH | D | 60 | 350 | 1.5 | 3323 | 93.0 |
| 98 | GH | W | 60 | 350 | 1.0 | 3207 | 90.1 |
| 159 | GH | L | 60 | 350 | 1.0 | N/A | 91.0 |
| 160 | GH | A | 60 | 350 | 1.0 | N/A | 93.0 |
| 26 | BT | D | 45 | 400 | 1.5 | N/A | 90.1 |
| 27 | BT | D | 45 | 400 | 1.8 | 2603 | 90.2 |
| 28 | BT | D | 45 | 400 | 2.0 | N/A | 90.9 |
| 30 | BT | D | 45 | 400 | 3.2 | 3399 | 90.6 |
| 34 | BT | D | 45 | 400 | 1.7 | 2262 | 90.7 |
| 35 | BT | D | 45 | 400 | 2.0 | 2143 | 91.4 |
| 76b | BT | D | 150 | 375 | 1.0 | 2154 | 90.5 |
| 105 | O | W | 60 | 350 | 1.0 | 1266 | 91.2 |
| 111 | O | W | 60 | 350 | 1.5 | 1123 | 90.1 |
| 112 | O | W | 60 | 375 | 1.5 | 1282 | 93.3 |
| 116 | O | W | 60 | 400 | 1.5 | 1458 | 93.5 |

a. Coals: FM-LS: Freedom Mine, North Dakota lignite, low sodium
FM-HS: Freedom Mine, North Dakota lignite, high sodium
GH: Glenharold Mine, North Dakota lignite
BT: Black Thunder Mine, Wyoming subbituminous
O: Ohio 11 Mine, Kentucky bituminous

b. Solvent: W = Wilsonville Run 262E V1074 composite distillate 343 °C x 565 °C
D = Wilsonville Run 262E V1074 composite distillate 343 °C x 510 °C cut
L = Lummus Pasting Solvent Distillate (Run 3LCF7)
A = Anthracene Oil (Reilly Industries)

c. HI = hydride ion reagent "A"

d. Pressure calculated at reaction temperature

e. Coal conversion to THF-solubles on moisture and $SO_3$-free-ash free basis

f. N/A = not available

TABLE 9

COAL CONVERSION AS A FUNCTION OF REACTION TEMPERATURE, HYDRIDE ION REAGENT/DRY COAL RATIO, AND RESIDENCE TIME FREEDOM MINE NORTH DAKOTA LIGNITE (LOW ASH)

| Run No. | Reaction Temp., °C | Hydride Ion Reagent/ Dry Coal | Residence Time, min | Coal Conversion, wt % |
|---|---|---|---|---|
| 11 | 400 | 1.1 | 45 | 90.4 |
| 10 | 375 | 1.1 | 45 | 81.9 |
| 7 | 350 | 1.1 | 45 | 73.8 |
| 18 | 400 | 1.4 | 45 | 90.4 |
| 5 | 375 | 1.4 | 45 | 91.0 |
| 4 | 350 | 1.4 | 45 | 72.2 |
| 90c | 400 | 1.1 | 150 | 91.4 |
| 60 | 375 | 1.1 | 150 | 92.4 |
| 93 | 350 | 1.1 | 150 | 86.2 |

TABLE 10

COAL CONVERSION AS A FUNCTION OF REACTION TEMPERATURE, HYDRIDE ION REAGENT/DRY COAL RATIO, AND RESIDENCE TIME BLACK THUNDER MINE SUBBITUMINOUS COAL

| Run No. | Reaction Temp., °C | Hydride Ion Reagent/ Dry Coal | Residence Time, min | Coal Conversion, wt % |
|---|---|---|---|---|
| 41 | 400 | 0.0 | 45 | 70.0 |
| 40 | 375 | 0.0 | 45 | 50.3 |
| 39b | 350 | 0.0 | 45 | 36.6 |
| 20 | 400 | 1.0 | 45 | 87.8 |
| 21 | 375 | 1.0 | 45 | 80.1 |
| 23 | 350 | 1.0 | 45 | 62.9 |
| 75 | 400 | 1.0 | 60 | 86.5 |
| 76 | 375 | 1.0 | 60 | 90.1(a) |
| 73 | 350 | 1.0 | 60 | 82.6 |

(a) Average of two determinations

TABLE 11

COAL CONVERSION AS A FUNCTION OF REACTION TEMPERATURE
OHIO 11 MINE BITUMINOUS COAL

| Run No. | Reaction Temp., °C | Hydride Ion Reagent/ Dry Coal | Residence Time, min | Coal Conversion, wt% |
|---|---|---|---|---|
| 116 | 400 | 1.0 | 60 | 93.4 |
| 112 | 375 | 1.0 | 60 | 93.3 |
| 104 | 350 | 1.0 | 60 | 88.8 |
| 122b | 300 | 1.0 | 60 | 38.2 |

TABLE 12

COAL CONVERSION AS A FUNCTION OF REACTION TEMPERATURE
AND HYDRIDE ION/DRY COAL RATIO
GLENHAROLD MINE LIGNITE

| Run No. | Reaction Temp., °C | Hydride Ion Reagent/ Dry Coal | Residence Time, min | Coal Conversion, wt% |
|---|---|---|---|---|
| 78 | 400 | 0.9 | 45 | 91.9 |
| 79 | 375 | 0.9 | 45 | 85.4 |
| 81 | 350 | 0.9 | 45 | 67.4 |
| 84 | 400 | 1.1 | 45 | 92.6 |
| 83b | 375 | 1.1 | 45 | 85.3 |
| 82 | 350 | 1.1 | 45 | 68.1 |

TABLE 13

COAL CONVERSION AS A FUNCTION OF HYDRIDE ION SOURCE
BLACK THUNDER MINE SUBBITUMINOUS COAL

Hydride Ion Reagent/dry Coal = 1.0
Solvent/dry Coal = 2.0
Residence Time = 45 min

| Reaction temperature, °C | Coal Conversion, wt % | |
|---|---|---|
| | Hydride Ion Source "A" | Hydride Ion Source "B" |
| 350 | 62.9 | 72.5 |
| 400 | 87.8 | 70.2 |

TABLE 14

COAL CONVERSION AS A FUNCTION OF HYDRIDE ION SOURCE
FREEDOM MINE NORTH DAKOTA LIGNITE (LOW ASH)

Hydride Ion/Dry Coal = 1.0
Solvent/Dry Coal = 2.2
Reaction Temperature = 350 °C
Residence Time = 60 min

| Coal Conversion, wt % | |
|---|---|
| Hydride Ion Source "A" | Hydride Ion Source "C" |
| 72.3<br>77.4 (a) | 77.1 (b)<br>75.2 (c)<br>75.6 (d)<br>75.1 (d) |

(a) slow heating rate
(b) HI "C" charged as a dry crystal
(c) HI "C"charged as a water solution
(d) HI "C" impregnated coal feed

TABLE 15

EFFECT OF SOLVENT TYPE ON COAL CONVERSION

Freedom Mine Lignite: 60 min; 350°C; HI "A"/Dry Coal = 1.1; Solvent/Dry Coal = 2.2

| Solvent (a) | W | D | RA | KAO | L | T |
|---|---|---|---|---|---|---|
| Coal Conversion, wt % | 69.9 | 72.3 | 82.8 | - | - | 66.8 |

Glenharold Mine Lignite: 60 min; 350°C; HI "A"/Dry Coal = 1.0; Solvent/Dry Coal = 2.0

| Solvent (a) | W | D | RA | KAO | L |
|---|---|---|---|---|---|
| Coal Conversion, wt % | 76.6 | 86.5 | 93.0 | 91.0 | 93.1 |

Black Thunder Mine Subbituminous: 60 min; 350°C; HI "A"/Dry Coal = 1.0; Solvent/Dry Coal = 2.1

| Solvent (a) | W | D | RA | KAO | L |
|---|---|---|---|---|---|
| Coal Conversion, wt % | 66.1 | ~67 (b) | 84.1 | - | 73.9 (c) |

(a) Solvent:

W = Wilsonville Run 262E, V1074
D = Wilsonville Run 262E, V1074, 488°C⁻ distillation fraction
L = Lummus Pasting Solvent disitillate, Run3LCF7
RA = Anthracene Oil manufactured by Reilly Industries
KAO= Anthracene Oil manufactured by Kawasaki Steel Corp.
T = Tetralin

(b) Extrapolated

(c) Average of two tests

TABLE 16

TEST OF RECYCLED PROCESS SOLVENT

Solvent: Wilsonville Run 262E V-1074 distillate recovered from one-liter autoclave tests Run 8-LA.

Hydride Ion "A"/dry coal = 1.0

| Coal | Temp, °C | Time, Min. | Coal Conversion, wt % | |
|---|---|---|---|---|
| | | | Fresh Solvent | Recycled Solvent |
| Black Thunder Mine | 350 | 150 | 82.6 | 81.1 |
| Black Thunder Mine | 400 | 45 | 88.8 | 87.2 |
| Black Thunder Mine | 375 | 150 | 89.7 | 88.4 |
| Glenharold Mine | 350 | 60 | 90.1 (a) | 81.5 (a) |
| Ohio 11 | 350 | 60 | 86.7 | 86.2 |

(a) Average of two tests.

TABLE 17

COAL CONVERSION AS A FUNCTION OF SOLVENT/DRY COALRATIO

Black Thunder Mine Subbituminous: 60 min; 350 °C; HI/Dry Coal = 1.0
Wilsonville Run 262E, V1067 Distillate

| Solvent/Dry Coal | Coal Conversion, wt % |
|---|---|
| 2.5 | 75.8 |
| 2.9 | 74.8 |
| 3.6 | 75.2 |

Black Thunder Mine Subbituminous: 60 min; 350 °C; HI/Dry Coal = 1.5
Wilsonville Run 262E, V1074 Distillate

| Solvent/Dry Coal | Coal Conversion, wt % |
|---|---|
| 2.4 | 81.4 |
| 3.6 | 81.8 |

Freedom Mine Lignite: 60 min; 350 °C; HI/Dry Coal = 1.1
Wilsonville Run 262E, V1074 Distillate

| Solvent/Dry Coal | Coal Conversion, wt % |
|---|---|
| 0 | 42.1 |
| 2.3 | 72.3 |

Glenharold Mine Lignite: 60 min; 350 °C; HI/Dry Coal = 1.5

| Solvent/Dry Coal | Coal Conversion, wt % | |
|---|---|---|
| | Lummus Run 3LCF Pasting Solvent | Wilsonville Run 262E, V10974 Distillate |
| 1.0 | 89.6 | - |
| 1.5 | 93.7 | 76.6 |
| 1.8 | - | 84.1 |
| 2.0 | 93.1 | 86.5 |
| 2.4 | - | 90.4 |

TABLE 18

WEATHERING OF BLACK THUNDER MINE COAL

Reaction Conditions: 60 min; 350 °C; HI "A"/Dry Coal = 1.5

| Run No. | Coal | Moisture Content, wt % | Conversion, wt % |
|---|---|---|---|
| 134 | As-Received | 22.0 | 73.5 |
| 118B | Weathered | 0.9 | 61.0 |
| 119 | Weathered | 0.9 | 66.1 |
| 110 | Water Added to As-Received | 38.0 (a) | 77.4 |

(a) Equivalent value: (Added water + coal moisture)/coal

TABLE 19

COMPARISON OF HIGH- AND LOW-SODIUM CONTENT
FREEDOM MINE LIGNITE

Solvent: Wilsonville 262E, V-1074; Solvent/Dry Coal: 2.2; HI "A"/Dry Coal = 1.1

| | Coal Conversion, wt % (a) | | | |
|---|---|---|---|---|
| | Time: 45 min | | Time: 60 min | |
| Temp., °C | High Na | Low Na | High Na | Low Na |
| 350 | 58.0 | 67.8 (b) | 65.2 | 73.9 (b) |
| 375 | 76.4 | 83.5 | | |

(a) Conversion on moisture and $SO_3$-free ash-free basis
b) Solvent/dry coal: 2.3

TABLE 20

MICROAUTOCLAVE TESTS
SODIUM ADDITION TO FREEDOM MINE, LOW-SODIUM LIGNITE

Solvent: Wilsonville 262E, V-1074; Solvent/Dry Coal: 2.2; HI "A"/Dry Coal = 1.1; 350 °C

| Na Added (as Reagent "C"), g | Total Na, as wt % Dry Coal | Coal Conversion, wt % (a) | |
|---|---|---|---|
| | | Time: 30 min | Time: 60 min |
| None | 0.11 | 58.9 (b) | 73.9 |
| 0.017 | 0.28 | 64.0 | 74.3 |
| 0.05 | 0.55 | 59.1 | 76.1 |

(a) Conversion on moisture and $SO_3$-free ash-free basis
(b) Slow heating rate, 30 min residence time at 350 °C

TABLE 21

MASS AND ELEMENTAL BALANCE DATA - MICROAUTOCLAVE TESTS

| | Black Thunder Mine Subbituminous Coal Run 73 | | Black Thunder Mine Subbituminous Coal Run 74b | | Black Thunder Mine Subbituminous Coal Run 76 | |
|---|---|---|---|---|---|---|
| Reaction Conditions | | | | | | |
| Time, min | 150 | | 45 | | 150 | |
| Temp, °C | 350 | | 400 | | 375 | |
| HI "A"/dry coal ratio | 1.0 | | 1.0 | | 1.0 | |
| Solvent/dry coal ratio | 2.1 | | 2.1 | | 2.1 | |
| Coal Conversion, wt % | 82.6 | | 88.8 | | 89.7 | |
| Mass Balance, % | 98.9 | | 95.4 | | 100.0 | |
| | Feed | Product | Feed | Product | Feed | Product |
| Fraction, wt % (a) | | | | | | |
| Gas | 0.0 | 14.4 | 0.0 | 16.6 | 0.0 | 15.5 |
| IBP-120 °C | 23.5 (HI "A") | 10.5 | 23.5 (HI "A") | 11.3 | 23.5 (HI "A") | 11.4 |
| | +5.8 ($H_2O$) | | +5.8 ($H_2O$) | | +5.8 ($H_2O$) | |
| | 29.3 | | 29.3 | | 29.3 | |
| 120-488 °C | 47.0 (Solvent) | 52.8 | 47.0 (Solvent) | 46.7 | 47.0 (Solvent) | 52.9 |
| 488 °C+ | 0 | | 0 | | 0 | |
| THF Insoluble | 21.9 (Coal, MAF) | 15.9 | 21.9 (Coal, MAF) | 16.9 | 21.9 (Coal, | 16.4 |
| | +1.3 (Ash) | 5.0 | +1.3 (Ash) | 3.7 | MAF) | 3.5 |
| | 23.2 | | 23.2 | | +1.3 (Ash) | |
| | | | | | 23.2 | |
| Elemental Balance, % | | | | | | |
| C | 96.5 | | 86.6 | | 96.2 | |
| H | 102.0 | | 96.2 | | 103.0 | |
| N | 86.7 | | 79.9 | | 94.5 | |
| S | 63.0 | | 40.1 | | 60.1 | |
| O | 91.0 | | 96.0 | | 93.2 | |
| Ash | 98.7 | | 107.0 | | 96.3 | |

| | Ohio 11 Mine Bituminous Coal Run 117 | | Glenharold Mine Lignite Run 127b | |
|---|---|---|---|---|
| Reaction Conditions | | | | |
| Time, min | 60 | | 60 | |
| Temp, °C | 350 | | 350 | |
| HI "A"/dry coal ratio | 1.0 | | 1.0 | |
| Solvent/dry coal ratio | 1.5 | | 2.4 | |
| Coal Conversion, wt % | 86.7 | | 92.0 | |
| Mass Balance, % | 95.5 | | 98.6 | |
| | Feed | Product | Feed | Product |
| Fraction, wt % (a) | | | | |
| Gas | 0.0 | 16.1 | 0.0 | 14.2 |
| IBP-120 °C | 28.6 (HI "A") | 10.4 | 20.4 (HI "A") | 17.6 |
| | +0.8 ($H_2O$) | | +10.3($H_2O$) | |
| | 29.4 | | 30.7 | |
| | 42.1 (Solvent) | 41.9 | 48.9 (Solvent) | 48.2 |
| 120-488 °C | 0 | | 0 | |
| 488 °C+ | 26.3 (Coal, MAF) | 21.4 | 28.4 (Coal, | 14.8 |
| THF Insoluble | +2.2 (Ash) | 5.5 | MAF) | 3.7 |
| | 28.5 | | +1.9 (Ash) | |
| | | | 20.3 | |
| Elemental Balance, % | | | | |
| C | 95.8 | | 100.3 | |
| H | 95.2 | | 102.6 | |
| N | 77.5 | | 96.2 | |
| S | 62.1 | | 49.1 | |
| O | 97.0 | | 92.6 | |
| Ash | 99.4 | | 102.3 | |

(a) Fractional product yield, wt % of feed

TABLE 22

COMPARISON OF COAL CONVERSION OBTAINED FOR DIFFERENT COALS AND QUANTITIES OF CARBON MONOXIDE AND HYDRIDE ION REAGENT "A"

Temperature 350 °C; Residence Time 60 min

| Coal (a) | CO or MF, Moles | Water (b)/ Dry Coal, g/g | Solvent (c)/ Dry Coal, g/g | CC, HI"A",(e) wt % | CC, CO(f), wt % |
|---|---|---|---|---|---|
| BT | 0.07 | 0.3 | 2.1 | 66.1 | 40.9 |
| BT | 0.09 | 0.3 | 2.1 | 73.5 | 41.2 |
| FM | 0.07 | 0.1 | 2.3 | 72.3 | 53.3 |
| FM | 0.13 | 0.1 | 1.4 | 82.1 | 54.6 |
| O | 0.08 | 0.3 | 1.5 | 90.1 | 56.5 |
| GH | 0.08 | 0.5 | 2.4 | 90.4 | 68.7 |
| GH | 0.09 | 0.5 | 1.5[d] | 93.7 | 67.0 |

(a) Coals: BT = Black Thunder Mine subbituminous
FM = Freedom Mine lignite, low ash
O = Ohio 11 Mine bituminous
GH = Glenharold Mine lignite

(b) Water includes coal moisture plus any added water
(c) Wilsonville Run 262, V1074 recycle solvent, 910°F-
(d) Lummus Pasting Solvent 3LCF7, distillate
(e) CC, HI"A" = coal conversion obtained with HI"A"
(f) CC, CO = coal conversion obtained with CO

TABLE 23

COAL CONVERSION (a) OBTAINED AT DIFFERENT RESIDENCE TIMES AND QUANTITIES OF CARBON MONOXIDE

Black Thunder Mine Subbituminous Coal
Temperature 350 °C;
Solvent: Wilsonville Run 262E, V1074, 910 °F-; Solvent/dry coal = 1.2

| Time, min | CO, moles | | | |
|---|---|---|---|---|
| | 0.01 | 0.05 | 0.07 | 0.09 |
| 30 | | | | 5.1 |
| 45 | | | | 30.6 |
| 60 | 28.6 | 33.2 | 38.1 | 38.8 |
| 90 | | | | 50.6 |
| 120 | | | | 57.1 |

(a) Coal Conversion defined as the weight percent of tetrahydrofuran solubles

TABLE 24

COAL CONVERSION WITH CO, CO/METHANOL, AND HI "A" AS LIQUEFACTION AGENTS

60 min, 350 °C

| Coal | Solvent (a) | Solvent/ Dry Coal | Hydride Ion/ Dry Coal | CO, moles | MeOH, moles | Coal Conversion, wt % | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | CO | CO/ MeOH | HI "A" |
| Glenharold Mine Lignite | L | 1.5 | 1.0 | 0.11 | 0.09 | 67.0 | 76.2 | 93.7 |
| Ohio 11 Mine Bituminous | WD | 1.5 | 1.0 | 0.15 | 0.13 | 56.5 | 70.2 | 90.1 |
| Freedom Mine Lignite | WD | 1.4 | 2.2 | 0.09 | 0.09 | 54.6 | 77.6 | 82.1 |

(a) L = Lummus Run 3LCF7 pasting solvent
WD = Wilsonville Run 262E, V1074 distillate

TABLE 25

MAXIMUM COAL CONVERSIONS
CO, $CO/H_20$, $CO/H_2$ REACTION SYSTEMS

| Ref No. | Coal | Agent | CO Pressure, MPa | Temp., °C | Time, min | Reaction Solvent | Coal: Solvent: Water | Extraction Solvent | Reactor Size, mL | Coal Conver-sion | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 6 | Bruceton hvab | $CO/H_2O$ | 10.3 | 425 | 10 | Phenanthrene | 1:1:0.5 | Benzene | 5 |
| 6 | Texas Lignite | $CO/H_2O$ | 10.3 | 390 | 10 | Phenanthrene | 1:1:0.5 | Benzene | 5 |
| 6 | ND Lignite | $CO/H_2O$ | 10.3 | 390 | 10 | Phenanthrene | 1:1:0.5 | Benzene | 5 |
| 7 | Bituminous | $CO/H_2O$ | 10 | 380 | 30 | None | 1:0:0.006 | Benzene | |
| 7 | Lignite | $CO/H_2O$ | 10 | 380 | 30 | None | | Benzene | |
| 8 | ND Lignite | $CO/H_2$ | 17.2 | 450 | | Gulf Oil FS-120 | | | |
| 8 | ND Lignite | $CO/H_2$ | 17.2 | 404 | | Gulf Oil FS-120 | | | |
| 9 | Illinois 6 | $CO/H_2$/KOH | 29.4 | 400 | 20 | None | | Pyridine} | 3 |
| | | | | | | | | Benzene} | |
| 10 | ND Lignite | $CO/H_2$ | 27.7 | 480 | 40 | Anthracene Oil | | | |
| 11 | ND Lignite | $CO/H_2$ | | 400 | 60 | Anthracene Oil | | | 3 |
| 11 | ND Lignite | $CO/H_2/H_2S$ | 26.5 | 420 | 20 | H-Anthracene Oil | | | 5 |
| 12 | Wakimoto | $CO/H_2$/CO-Mo | 4 | 300 | 60 | Oil (230-300 °C) | 1:10:2.2 | Pyridine | 1 |
| 12 | Kurikomo | $CO/H_2$/CO-Mo | 4 | 300 | 60 | Oil (230-300 °C) | 1:10:2.2 | Pyridine | 1 |
| 13 | Illinois 6 | $CO/H_2$/KOH | 7 | 400 | 60 | None | 1:0:3.6 | Benzene | 3 |
| 14 | Texas Lignite | $CO/H_2O$ | 6.9 | 380 | 60 | Coal-Derived Recycle | | THF | 2 |
| 14 | Wyodak Subbit | $CO/H_2O$ | 6.9 | 380 | 60 | Oil | | THF | 2 |
| 14 | Ohio Bituminous | $CO/H_2O$ | 6.9 | 380 | 60 | Coal-Derived Recycle | | THF | 2 |
| 15 | Illinois 6 | $CO/H_2$/KOH | 34.4 | 400 | 20 | Oil | 1:0:6 | Toluene | 3 |
| 15 | Illinois 6 | $CO/H_2$/KOH | 34.4 | 400 | 20 | Coal-Derived Recycle | 1:0:6 | Toluene | 3 |
| 16 | Illinois 6 | $CO/H_2O$ | 4 | 400 | 60 | Oil | | THF} | 3 |
| | | | | | | None | | Toluene} | |
| 17 | Waterberg | $CO/H_2O$ | 6 | 400 | 30 | None | | THF | 10 |
| 17 | Waterberg | $CO/H_2O$/Pyrite | 6 | 400 | 30 | None | | THF | 10 |
| 17 | Waterberg | $CO/H_2O/H_2S$ | 6 | 400 | 30 | | | THF | 10 |
| 17 | Waterberg | $CO/H_2O/H_2S$/Pyrite | 6 | 400 | 30 | None | | THF | 10 |
| 17 | Waterberg | $CO/H_2O$/Pyrite/S | 6 | 400 | 30 | None | | THF | 10 |
| 18 | Sulcis Subbit | $CO/H_2O/Na_2CO_3$ | 4 | 400 | 60 | None | | THF | 3 |
| 19 | Callide | $CO/H_2O/Na_2CO_3$ | 3 | 405 | 60 | None | | $CH_2CL_2$ | 1 |
| 19 | Morwell | $CO/H_2O/Na_2CO_3$ | 3 | 405 | 60 | None | | $CH_2CL_2$ | 1 |
| 19 | Greta | $CO/H_2O/Na_2CO_3$ | 3 | 405 | 60 | None | | $CH_2CL_2$ | 1 |
| 19 | PSOC 1098 | $CO/H_2O/Na_2CO_3$ | 3 | 405 | 60 | None | | $CH_2CL_2$ | 1 |
| 19 | Burning Star | $CO/H_2O/Na_2CO_3$ | 3 | 405 | 60 | None | | $CH_2CL_2$ | 1 |
| 20 | Yallourn | $CO/H_2O$ | 7 | 375 | 60 | None | | THF | 5 |
| 20 | Yallourn | $CO/H_2O/Fe(CO)_5$ | 7 | 375 | 60 | None | | THF | 5 |
| 20 | Yallourn | $CO/H_2O/Fe(CO)_5$/S | 7 | 375 | 60 | None | | THF | 5 |
| 21 | Brown Coal | $CO/H_2O/NAALO_2$ | 3 | 375 | 30 | 1-methylnaphthalene | 1:0:3 | THF | 5 |
| 21 | Brown Coal | $CO/H_2O/NAALO_2$ | 3 | 375 | 30 | 1-methylnaphthalene | 1:0:3 | THF | 5 |
| 22 | Black Thunder | $CO/H_2O/K_2CO_3$ | 2.8 | 410 | 30 | 1-methylnaphthalene | | THF | 10 |
| 23 | Wyoming Subbit | CO | 3 | 365 | 30 | None | | $CH_2CL_2$ | 3 |
| | | | | | | None | | | |
| | | | | | | None | | | |
| | | | | | | None | | | |

TABLE 26

ONE-LITER AUTOCLAVE TESTS

| Run No. | Feed Coal (a) | Solvent (b) | Reaction Temp., °C | Residence Time, min | HI/dry coal Ratio | Solvent/ dry coal Ratio | Coal Conv., wt % (c) | Coal Conv., wt % (d) |
|---|---|---|---|---|---|---|---|---|
| 2 - LA | BT | D | 400 | 45 | 1.0 | 2.0 | N/A | 88.8 |
| 3 - LA | BT | D | 400 | 45 | 1.0 | 1.5 | N/A | N/A |
| 4 - LA | BT | D | 400 | 45 | 1.0 | 1.5 | 84.0 | 88.8 |
| 4b - LA | BT | D | 400 | 45 | 1.0 | 1.5 | 84.0 (e) | 88.8 |
| 5 - LA | BT | D | 350 | 150 | 1.0 | 1.5 | 84.4 | 82.6 |
| 6 - LA | O | D | 350 | 60 | 1.0 | 1.5 | 88.8 | 86.7 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 7 - LA | FM-HS | D | 350 | 60 | 1.5 | 2.5 | 86.3 | 83.2 |
| 8 - LA | GH | D | 350 | 60 | 1.0 | 2.4 | 93.4(f) | 90.1 |
| 9 - LA(g) | GH | L | 350 | 60 | 1.0 | 2.4 | 92.9(f) | 93.1 |
| 9a - LA | GH | L | 350 | 60 | 1.0 | 1.5 | N/A | 93.7 |

(a) Coals: BT - Black Thunder Mine, Wyoming Subbituminous
O - Ohio 11 Mine, Kentucky Bituminous
FM-HS - Freedom Mine, North Dakota Lignite, High Sodium Sample
GH - Glenharold Mine, North Dakota Lignite

(b) Solvents: D - Wilsonville Run 262E V1074, distillate
L - Lummus pasting solvent distillate Run 3LCF7

(c) Coal Conversion to THF-solubles on $SO_3$-free-ash-free coal basis; determined from ca. 10 g aliquots using ash balance methods

(d) Corressponding microautoclave test coal conversion

(e) Determined by UK/CAER

(f) determined from THF-filtration of entire product

(g) solvent/dry coal = 2.4

TABLE 27

MASS AND ELEMENTAL BALANCE DATA
GLENHAROLD MINE LIGNITE
(Run No. 8-LA)

Reaction Conditions: 60 min; 350 °C
HI "A"/dry coal = 1.0
solvent/dry coal = 2.4

Coal Conversion, wt % 93.4

| Fraction, wt % (a) | Feed | Product |
|---|---|---|
| Gas | 0.0 | 8.7 |
| IBP-120 °C | 20.3 (HI "A")<br>+10.4 ($H_2O$)<br>30.7 | 12.3 |
| 120-488 °C | 49.0 (Solvent) | 47.2 |
| 488 °C$^+$ | 0<br>18.4 (Coal, MAF) | 13.8 |
| THF-Insoluble | 1.9 (Ash)<br>20.3 | 3.1 |

(a) Fractional product yield, wt % of feed

Mass Balance, % 85.1

Elemental Balance, %

| | |
|---|---|
| C | 90.9 |
| H | 89.3 |
| N | 96.4 |
| S | 53.4 |
| O | 53.1 |
| ash | 95.3 |

TABLE 28

ANALYSES OF 488 °C$^+$ FRACTION

| | Black Thunder Mine Subbituminous Coal Run 73 | | Black Thunder Mine Subbituminous Coal Run 74b | | Black Thunder Mine Subbituminous Coal Run 76 | |
|---|---|---|---|---|---|---|
| Reaction Conditions | | | | | | |
| Time, min | 150 | | 45 | | 150 | |
| Temp, °C | 350 | | 400 | | 375 | |
| HI "A"/dry coal ratio | 1.0 | | 1.0 | | 1.0 | |
| Solvent/dry coal ratio | 2.1 | | 2.1 | | 2.1 | |
| Coal Conversion, wt % | 82.6 | | 88.8 | | 89.7 | |
| Mass Balance, % | 98.9 | | 95.4 | | 100.0 | |
| | Feed | 400 °C$^+$ | Feed | 400 °C$^+$ | Feed | 400 °C$^+$ |
| Elemental Balance, % | | | | | | |
| C | 74.44 | 83.00 | 74.44 | 86.43 | 74.44 | 85.41 |
| H | 4.95 | 6.84 | 4.95 | 6.42 | 4.95 | 6.54 |
| N | 1.10 | 1.01 | 1.10 | 0.97 | 1.10 | 1.00 |
| S | 0.53 | 0.20 | 0.53 | 0.23 | 0.53 | 0.14 |
| O (by difference) | 18.98 | 8.95 | 18.98 | 6.04 | 18.98 | 6.91 |
| Molar H/C | 0.80 | 0.98 | 0.80 | 0.89 | 0.80 | 0.91 |
| Molar O/C | 0.19 | 0.08 | 0.19 | 0.05 | 0.19 | 0.06 |

| | Ohio 11 Mine Bituminous Coal Run 117 | | Glenharold Mine Lignite Run 127b | |
|---|---|---|---|---|
| Reaction Conditions | | | | |
| Time, min | 60 | | 60 | |
| Temp, °C | 350 | | 350 | |
| HI "A"/dry coal ratio | 1.0 | | 1.0 | |
| Solvent/dry coal ratio | 1.5 | | 2.4 | |
| Coal Conversion, wt % | 86.7 | | 92.0 | |
| Mass Balance, % | 95.5 | | 98.6 | |
| | Feed | 400 °C$^+$ | Feed | 400 °C$^+$ |
| Elemental Balance, % | | | | |
| C | 80.88 | 83.49 | 69.66 | 83.34 |
| H | 5.55 | 5.87 | 4.9 | 7.34 |
| N | 1.64 | 1.32 | 1.04 | 1.15 |
| S | 3.31 | 1.30 | 1.47 | 0.43 |
| O (by difference) | 8.52 | 8.02 | 22.93 | 7.73 |
| Molar H/C | 0.82 | 0.84 | 0.84 | 1.06 |
| Molar O/C | 0.07 | 0.08 | 0.25 | 0.07 |

TABLE 29

ANALYSIS OF 488 °C$^+$ FRACTION
GLENHAROLD MINE LIGNITE
(Run No. 8-LA)

Reaction Conditions: 60 min; 350 °C
HI "A"/dry coal = 1.0
solvent/dry coal = 2.4

Yield of 488 °C$^+$, wt % of feed = 18.1

| Elemental Analyses, wt % MAF | 488 °C$^+$ | Feed Coal |
|---|---|---|
| C | 83.58 | 69.66 |
| H | 6.75 | 4.90 |
| N | 1.22 | 1.04 |
| S | 0.43 | 1.47 |
| O (by difference) | 8.02 | 22.93 |
| Molar H/C | 0.96 | 0.84 |
| Molar O/C | 0.07 | 0.25 |

TABLE 30

SOLVENT FRACTIONATION OF THE 488 °C$^+$ FRACTION OF HYDRIDE ION (a) PROMOTED COAL LIQUEFACTION PRODUCTS

| Run No. | Coal (b) | Temp., °C | Solvent(c)/ Dry Coal | Conv., wt% | Wt% MAF Coal Feed | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | 488 °C$^+$ | Oils | Asphal-tenes | Preasphal-tenes |
| 8-LA | GH | 350 | 2.4 | 93.4 | 74.9 | 29.2 | 15.7 | 30.0 |
| 127B | GH | 350 | 2.4 | 90.4 | 72.8 | 28.2 | 11.9 | 32.8 |
| 143 | GH | 350 | 1.5 | 76.6 | 55.8 | 16.5 | 11.5 | 27.8 |
| 73 | BT | 350 | 2.1 | 82.6 | 71.6 | 26.1 | 15.6 | 29.9 |
| 74B | BT | 400 | 2.1 | 88.8 | 75.9 | 34.4 | 18.2 | 23.3 |
| 76B | BT | 375 | 2.0 | 90.5 | 73.8 | 25.9 | 22.8 | 23.1 |

(a). Hydride ion reagent: "A"
(b) Coals: BT = Black Thunder Mine subbituminous
GH = Glenharold Mine lignite
(c) Wilsonville Run 262, V1074 recycle solvent, 910°F$^-$

# TABLE 31
# SAMPLE PREPARATION FOR FILTRATION

| Run No. | Run Temp., °C | Run Time, min | s/c Ratio, db | NCF No. | Procedure Employed in Preparation for Filtration |
|---|---|---|---|---|---|
| Freedom Mine Lignite | | | | | |
| 4a | 350 | 45 | 1.6 | 5 | |
| 4b | 350 | 45 | 1.6 | 6 | |
| 10a | 375 | 45 | 1.6 | 3 | dried in oven at 65 °C and 130 °C |
| 10b | 375 | 45 | 1.6 | 4 | mixed cold and fed to microfilter |
| 11a | 400 | 45 | 1.6 | 2 | |
| 11b | 400 | 45 | 1.6 | 7 | |
| 7LA | 350 | 60 | 2.3 | 22 | at 135 °C inhomogeneous; mixed better at 250 °C, fed to 200 mL filter |
| Glenharold Lignite | | | | | |
| 8a + b LA | 350 | 60 | 2.3 | 28 | two-phase material even at 250 °C (evap loss at 2135 °C was 2.3%) |
| 8a + b LA | 350 | 60 | 2.3 | 29 | decanted into two phases at 250 °C (18% 'heavies' and 72% 'lights') |
| 8a + b LA | 350 | 60 | 2.3 | 30 | attempted to recombine in same ratio for filtration |
| 8a + b LA | 350 | 60 | 2.3 | 31 | samples not well mixed, no reliable data |
| 8a + b LA | 350 | 60 | 2.3 | 32 | |
| 8a + b LA | 350 | 60 | 2.3 | 37 | heavies mixed with a coal tar dist. at 200 °C (ratio 1:1); fed to 200 mL filter |
| 8c LA | 350 | 60 | 2.3 | 34 | two-phase material, separated at 65 °C (35% heavies, 65% lights) |
| 8c LA | 350 | 60 | 2.3 | 35 | sample of heavies fed to microfilter (2 tests) |
| 8c LA | 350 | 60 | 2.3 | 36 | sample of heavies blended with coal tar dist (1:1.5) fed to 200 mL filter |
| 8c LA | 350 | 60 | 2.3 | 39 | sample of heavies blended with coal tar dist (1:1) fed to 200 mL filter |
| 8c LA | 350 | 60 | 2.3 | 40 | sample o f heavies blended with coal tar dist (1.5:1) fed to 200 mL filter |
| 8c LA | 350 | 60 | 2.3 | 41 | sample of heavies blended with coal tar dist (2:1) fed to 200 mL filter |
| 8c LA | 350 | 60 | 2.3 | 42 | sample of heavies blended with coal tar dist (3:1) fed to 200 mL filter |
| 9a LA* | 350 | 60 | 1.5 | 43 | 0.6, 4.8, 9.8% lights evap. at 65, 135, and 150 °C fed to 200 mL filter |
| Black Thunder Subbituminous Coal | | | | | |
| 22c | 350 | 45 | 2.1 | 12 | |
| 21 | 375 | 45 | 2.0 | 9 | |
| 21d | 375 | 45 | 2.0 | 11 | |
| 26a | 400 | 45 | 2.1 | 8 | dried in oven at 65 °C and 135 °C |
| 26b | 400 | 45 | 2.1 | 10 | mixed cold and fed to microfilter |
| 53a | 400 | 45 | 1.5 | 13 | |
| 53b | 400 | 45 | 1.5 | 16 | |
| 52a | 400 | 45 | 1.0 | 14 | |
| 52b | 400 | 45 | 1.0 | 15 | |
| 4 LA | 400 | 45 | 1.5 | 20 | mixed cold and fed to 200 mL filter |
| 5 LA | 350 | 150 | 1.5 | 18a | mixed cold and split into 2 parts. Part a fed to 200 mL filter |
| 5 LA | 350 | 150 | 1.5 | 18b | Part b stripped of lights (13%), residue fed hot to 200 mL filter |
| Ohio 11 Bituminous Coal | | | | | |
| 123 | 300 | 60 | 1.5 | - | filtration not attempted |
| 128 | 370 | 60 | 1.5 | 27 | |
| 129a | 380 | 60 | 1.5 | 23 | |
| 129b | 380 | 60 | 1.5 | 24 | dried in oven at 65 °C and 135 °C |
| 130a | 390 | 60 | 1.5 | 25 | mixed cold and fed to microfilter |
| 130b | 390 | 60 | 1.5 | 26 | |
| 121a | 400 | 60 | 1.5 | 21 | |
| 121b | 400 | 60 | 1.5 | 33 | |
| 6LA | 350 | 60 | 1.5 | 19 | filtration aborted |

Notes: solvent used was Wilsonville R262E V1074 (488 °C) except where indicated
*solvent used was Lummus pasting solvent (3LCF7)

| Coal Mine | | Freedom | Glenharold | Black Thunder | Ohio 11 |
|---|---|---|---|---|---|
| moisture | % | 20.7 | 11.9 | 22.4 | 2.1 |
| ash content | % db | 5.8 | 12.0 | 6.7 | 6.9 |
| $SO_3$ in ash | % | 23.0 | 21.2 | 17.3 | 6.9 |
| ash ($SO_3$ free) | % db | 4.5 | 9.5 | 5.5 | 6.7 |
| ash content | % ar | 4.8 | 10.7 | 5.5 | 6.7 |
| ash ($SO_3$ free) | % ar | 3.7 | 8.5 | 4.5 | |

## TABLE 32

## MASS BALANCE AND FILTRATION DATA - FREEDOM MINE LIGNITE

| NCF No. | wt received | Drying loss (g) | Drying loss (%) | Dried wt (g) | Coal feed(ar) (g) | Coal feed(db) (g) | Coal feed(daf) (g) | Coal* feed(daf) (g) | Solvent feed (g) | Slurry feed (g) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | | | | | | | | | |
| 5 | 13.48 | 3.08 | 22.8 | 10.40 | 5.0 | 3.97 | 3.73 | 3.78 | 6.34 | 11.34 |
| 6 | 12.92 | 2.79 | 21.6 | 10.13 | 5.0 | 3.97 | 3.73 | 3.78 | 6.34 | 11.34 |
| 3 | 12.69 | 2.59 | 20.4 | 10.10 | 5.0 | 3.97 | 3.73 | 3.78 | 6.34 | 11.34 |
| 4 | 12.65 | 2.53 | 20.0 | 10.12 | 5.0 | 3.97 | 3.73 | 3.78 | 6.34 | 11.34 |
| 2 | 12.16 | 2.57 | 21.1 | 9.59 | 5.0 | 3.97 | 3.73 | 3.78 | 6.34 | 11.34 |
| 7 | 12.87 | 2.63 | 20.4 | 12.24 | 5.0 | 3.97 | 3.73 | 3.78 | 6.34 | 11.34 |
| 22 | 218.1 | 3.6 | 1.7 | 214.5 | 62.4 | 49.5 | 46.5 | 47.2 | 133.7 | 196.11 |

| NCF No. | Filter input (g) | Mass balance (%) | Filtrate yield (%) | Cake yield (%) | Cake THFI (%) | Solids in feed (%) | Filtration Temp ( C) | Filtration Pressure (psig) | Viscosity @250 C (m Pas) | Cake# resistivity (m/kg) (x 10^10) | total flow after 30 min (kg/m2) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 5.6 | 85.6 | 60.2 | 25.3 | 71.6 | 18.1 | 250 | 30 | 0.3 | too fast | |
| 5 | 9.4 | 98.7 | 52.6 | 46.2 | 28.0 | 12.9 | 167 | 2 | 0.3 | 1 | 166 |
| 6 | 8.2 | 92.5 | 45.9 | 46.6 | 28.5 | 13.3 | 200 | 30 | 0.3 | n/m | n/m |
| 3 | 8.3 | 95.6 | 62.9 | 32.7 | n/m | n/m | 235 | 30 | 0.4 | too fast | n/m |
| 4 | 8.5 | 99.8 | 68.8 | 31.0 | 29.7 | 9.2 | 247 | 30 | 0.4 | 2 | 976 |
| 2 | 7.9 | 95.0 | 79.6 | 14.8 | 32.2 | 4.8 | 268 | 30 | 0.8 | too fast | n/m |
| 7 | 6.2 | 93.5 | 77.0 | 10.4 | 47.9 | 5.0 | 230 | 30 | 0.8 | <17 | 266 |
| 22 | 196 | 98.7 | 91.3 | 7.4 | 72.6 | 5.4 | 275 | 15 | 15@ | 1.3 | 221 |

| NCF No | Filter cake analysis** | | | | $SO_3$ in ash (%) | ash enrich. factor | ash enrich. factor ($SO_3$-free basis) | coal conversion (1) from THFI | | coal conversion (2) from ash enrich. | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | H2O (%) | ash (%) | ash* (%) | VM (%) | | | | (% daf) | (% daf) | (% daf) | (% daf) |
| 1 | 4.12 | 3.47 | - | 58.2 | n/m | - | - | - | - | - | - |
| 5 | 0.08 | 4.29 | - | 73.4 | n/m | 0.74 | 0.96 | 70.1 | 68.6 | 66.1 | 73.9 |
| 6 | 0.17 | 4.16 | - | 72.9 | n/m | 0.72 | 0.93 | 70.1 | 68.6 | 64.3 | 72.5 |
| 3 | n/m | n/m | - | n/m | n/m | n/m | n/m | n/m | n/m | n/m | n/m |
| 4 | 0.56 | 5.69 | - | 61.7 | n/m | 0.98 | 1.28 | 81.2 | 79.7 | 74.7 | 80.5 |
| 2 | 0.30 | 10.45 | - | 69.1 | n/m | 1.80 | 2.34 | 93.9 | 92.5 | 87.4 | 90.3 |
| 7 | 0.12 | 15.59 | - | 56.7 | n/m | 2.69 | 3.50 | 92.5 | 91.1 | 87.3 | 90.2 |
| 22 | 2.41 | 32.2 | - | - | n/m | 5.56 | 7.22 | - | - | 92.7 | 94.4 |

* $SO_3$-free basis **analyses made prior to vacuum drying n/m = not measured @ from softening point # constant rate filtration

(1) Coal conversion = 100 - %solids x (dried digest wt - ash) / (daf coal)
(2) Coal conversion = 100 - [{%cake insol - %(cake H2O + ash)} x 100 / (ash enrich)x(100 - coal ash))}

# TABLE 33

## MASS BALANCE AND FILTRATION DATA - GLENHAROLD LIGNITE

| NCF No. | Filter input (g) | Mass balance (%) | Filtrate yield (%) | Cake yield (%) | Cake THFI (%) | Solids in feed (%) | Filtration Temp ( C) | Filtration Pressure (psig) | Viscosity @250 C (m Pas) | Cake resistivity (m/kg) (x 10^10) | Total flow after 30 min (kg/m2) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 8a + b LA | | | | | | | | | | | |
| 28 | 48 | 93 | | | | | 290 | 15.0 | n/m | - | - |
| 29 | 51 | 85 | | | | | 300 | 15.0 | n/m | - | - |
| 30 | 98 | 71 | no reliable data | | | | 330 | 15.0 | n/m | - | - |
| 31 | 95 | 62 | | | | | 320 | gravity | n/m | - | - |
| 32 | 95 | 71 | | | | | 330 | 10.0 | n/m | - | - |
| 37 | 100 | 95 | 61.8 | 33.3 | 42 | 14.0 | 310 | 14.0 | 20 | 2 | 290 |
| 8c LA | | | | | | | | | | | |
| 34 | 8.8 | 91 | 50.1 | 41.1 | 43 | 17.6 | 270 | 50.0 | 3300 | 4 | 16 |
| 35 | 3.2 | 97 | 77.6 | 19.4 | 56 | 10.9 | 300 | 50.0 | 5000 | - | - |
| 36 | 24.4 | 100 | 88.0 | 12.0 | 44 | 5.3 | 270 | 15.0 | n/m | 71 | 83 |
| 39 | 28.4 | 92 | 79.9 | 11.6 | 59 | 6.9 | 280 | 14.0 | 2.1 | 46 | 64 |
| 40 | 23.5 | 91 | 75.5 | 15.5 | 53 | 8.3 | 280 | 14.3 | 2.9 | 55 | 41 |
| 41 | 20.9 | 94 | 75.2 | 18.8 | 49 | 9.2 | 286 | 14.3 | 3.6 | 49 | 31 |
| 42 | 18.2 | 95 | 78.0 | 17.0 | 66 | 11.2 | 285 | 15 / 30 | 8.3 | 79 | 19 |
| 9a LA | | | | | | | | | | | |
| 43 | 179 | 93 | 80.2 | 12.5 | 60 | 7.5 | 253 | 50.0 | 0.9 | 183 | 93 |

| NCF No. | Filter cake analysis** | | | | $SO_3$ in ash (%) | ash enrich. factor | ash enrich. factor ($SO_3$-free basis) | coal conversion (2) from ash enrichment | |
|---|---|---|---|---|---|---|---|---|---|
| | cake $H_2O$ (%) | THFI ash (%) | cake ash* (%) | cake ash* (%) | | | | (% daf) | (% daf) |
| 8a + b LA | | | | | | | | | |
| 28 | 5.3 | - | 35.5 | 35.5 | n/m | 2.95 | 3.74 | n/m | n/m |
| 37 | 0.3 | - | 16.4 | 16.4 | n/m | 1.37 | 1.73 | no reliable data | |
| 8c LA | | | | | | | | | |
| 39 | 3.4 | 56.8 | 33.5 | 33.5 | n/m | 2.79 | 3.53 | 91.0 | 92.9 |
| 40 | 3.7 | 55.5 | 29.6 | 27.7 | 6.4 | 4.61 | 2.92 | 95.0 | 92.2 |
| 41 | 2.8 | 55.7 | 27.2 | 27.2 | n/m | 4.63 | 2.87 | 95.4 | 92.5 |
| 42 | 3.1 | 53.0 | 35.1 | 32.8 | 6.3 | 4.41 | 3.46 | 92.8 | 90.8 |
| 9a LA | | | | | | | | | |
| 43 | n/m | 53.4 | 32.1 | 32.1 | n/m | 4.44 | 3.38 | 92.8 | 90.6 |

*$SO_3$-free basis **analysis made prior to vacuum drying n/m = not measured

## TABLE 34

## MASS BALANCE AND FILTRATION DATA - BLACK THUNDER SUBBITUMINUOS COAL

| NCF No. | wt received | Drying loss (g) | Drying loss (%) | Dried wt. (g) | Coal feed(ar) (g) | Coal feed(db) (g) | Coal feed(daf) (g) | Coal* feed(daf) (g) | Solvent feed (g) | Slurry feed (g) |
|---|---|---|---|---|---|---|---|---|---|---|
| 12 | 13.71 | 2.29 | 16.7 | 11.42 | 5.00 | 3.88 | 3.61 | 3.65 | 8.00 | 13.00 |
| 9 | 13.76 | 2.03 | 14.8 | 11.73 | 5.00 | 3.88 | 3.61 | 3.65 | 8.00 | 13.00 |
| 11 | 13.66 | 2.43 | 17.8 | 11.23 | 5.00 | 3.88 | 3.61 | 3.65 | 8.00 | 13.00 |
| 8 | 12.08 | 2.21 | 18.3 | 9.87 | 4.47 | 3.47 | 3.22 | 3.27 | 7.15 | 11.62 |
| 10 | 12.31 | 2.39 | 19.4 | 9.92 | 4.47 | 3.47 | 3.22 | 3.27 | 7.15 | 11.62 |
| 13 | 10.60 | 2.60 | 24.5 | 7.00 | 4.47 | 3.47 | 3.22 | 3.27 | 5.36 | 9.83 |
| 16 | 10.30 | 2.38 | 23.1 | 7.92 | 4.47 | 3.47 | 3.22 | 3.27 | 5.36 | 9.83 |
| 14 | 8.88 | 2.55 | 28.7 | 6.33 | 4.47 | 3.47 | 3.22 | 3.27 | 3.58 | 8.05 |
| 15 | 8.80 | 2.62 | 29.8 | 6.18 | 4.47 | 3.47 | 3.22 | 3.27 | 3.58 | 8.05 |
| 20 | 74.4 | - | - | 74.4 | 33.6 | 26.1 | 24.2 | 24.6 | 40.8 | 74.4 |
| 18a | 83.5 | 11.8 | 14.1 | 71.7 | 32.6 | 14.8 | 23.5 | 23.8 | 39.1 | 71.7 |
| 18b | 80.9 | 10.3 | 12.7 | 70.6 | 32.1 | 14.6 | 23.1 | 23.5 | 38.5 | 70.6 |

| NCF No. | Filter input (g) | Mass balance (%) | Filtrate yield (%) | Cake yield (%) | Cake THFI (%) | Solids in feed (%) | Filtration Temp ( C) | Filtration Pressure (psig) | Assumed Viscosity @250°C (m Pas) | Cake# resistivity (m/kg) (x 10^10) | Total flow after 30 min (kg/m2) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 12 | 10.71 | 97.7 | 54.6 | 43.0 | 39.1 | 16.8 | 260 | 29.5 | 1 | 2 | 400 |
| 9 | 4.78 | 90.0 | 53.0 | 37.0 | 42.4 | 15.7 | 258 | 9.7 | 1 | 19 | 96 |
| 11 | 9.20 | 97.9 | 71.3 | 26.6 | 43.5 | 11.6 | 250 | 9.4 | 1 | 10 | 128 |
| 8 | 8.52 | 98.4 | 86.0 | 12.4 | 41.9 | 5.2 | 250 | 2.5 | 1 | 4 | 164 |
| 10 | 7.46 | 97.7 | 84.7 | 13.0 | 49.8 | 6.5 | 252 | 10.6 | 1 | 5 | 274 |
| 13 | 6.50 | 97.8 | 81.8 | 16.0 | 49.2 | 7.9 | 250 | 9.9 | 1 | 11 | 160 |
| 16 | 7.20 | 98.6 | 87.5 | 11.1 | 60.1 | 6.7 | 283 | 10.0 | 1 | 9 | 200 |
| 14 | 6.03 | 99.3 | 81.3 | 18.1 | 52.6 | 9.5 | 255 | 10.2 | 1 | 25 | 98 |
| 15 | 6.10 | 100 | 82.0 | 18.0 | 52.1 | 9.4 | 256 | 10.0 | 1 | 18 | 115 |
| 20 | 72.2 | 93.1 | 72.9 | 20.2 | 58.7 | 11.9 | 275 | 14.3 | 1 | 5 | 219 |
| 18a | 66.0 | 98.9 | 68.1 | 31.9 | 32.4 | 10.3 | 160 | 11.5 | 1 | 64 | 62 |
| 18b | 69.8 | 96.8 | 80.4 | 16.5 | 49.9 | 8.2 | 280 | 14.0 | 1 | 3 | 370 |

TABLE 34 (continued)

MASS BALANCE AND FILTRATION DATA - BLACK THUNDER SUBBITUMINOUS COAL

| NCF No. | Filter cake analysis** | | | | $SO_3$ in ash (%) | ash enrich. factor | ash enrich. factor ($SO_3$-free basis) | coal conversion (1) from THFI | | coal conversion (2) from ash enrich. | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $H_2O$ (%) | ash (%) | ash* (%) | VM (%) | | | | (% daf) | (% daf) | (% daf) | (% daf) |
| 12 | 0.15 | 5.00 | 4.59 | 71.4 | 8.1 | 0.75 | 0.83 | 52.2 | 51.0 | 51.3 | 56.2 |
| 9 | 0.40 | 9.83 | 8.96 | 59.6 | 8.9 | 1.47 | 1.62 | 54.5 | 53.3 | 76.5 | 78.7 |
| 11 | 0.58 | 8.87 | 7.54 | 67.1 | 15.0 | 1.33 | 1.36 | 70.0 | 68.7 | 72.5 | 73.2 |
| 8 | 0.47 | 15.83 | 14.33 | 63.6 | 9.5 | 2.37 | 2.59 | 90.7 | 89.4 | 88.4 | 89.4 |
| 10 | 0.37 | 17.93 | 16.16 | 58.1 | 9.9 | 2.68 | 2.92 | 86.5 | 85.3 | 87.4 | 88.4 |
| 13 | 0.25 | 17.35 | 15.91 | 58.9 | 8.3 | 2.59 | 2.87 | 86.8 | 85.5 | 86.9 | 88.2 |
| 16 | 0.01 | 22.54 | 20.27 | 50.5 | 10.1 | 3.37 | 3.66 | 90.0 | 88.8 | 88.1 | 89.0 |
| 14 | 0.11 | 18.15 | 16.56 | 52.1 | 8.8 | 2.71 | 2.99 | 87.4 | 86.2 | 86.4 | 87.7 |
| 15 | 0.17 | 18.27 | 16.46 | 53.3 | 9.9 | 2.73 | 2.97 | 88.1 | 86.9 | 86.8 | 87.9 |
| 20 | 0.78 | 15.12 | 13.62 | 57.0 | 9.9 | 2.26 | 2.46 | - | - | 79.7 | 81.4 |
| 18a | 0.59 | 7.41 | 7.41 | n/m | n/m | 1.11 | 1.34 | - | - | 76.4 | 80.5 |
| 18b | 0.91 | 11.05 | 11.05 | n/m | n/m | 1.65 | 2.00 | - | - | 75.4 | 79.6 |

* $SO_3$ free basis **analysis made prior to vacuum drying n/m = not measured # constant rate data

(1)coal conversion = 100 - %solids x (dried digest wt - ash) / (daf coal)
(2)coal conversion = 100 - [{%cake insol - %(cake H2O + ash)} x 100 / (ash enrich)x(100 - coal ash))}

## TABLE 35

## MASS BALANCE AND FILTRATION DATA - OHIO No. 11 BITUMINOUS COAL

| NCF No. | wt received | Drying loss (g) | Drying loss (%) | Dried wt. (g) | Coal feed(ar) (g) | Coal feed(db) (g) | Coal feed(daf) (g) | Solvent feed (g) | Slurry feed (g) |
|---|---|---|---|---|---|---|---|---|---|
| 27 | 13.6 | 1.9 | 14.0 | 11.7 | 5.0 | 4.9 | 4.56 | 7.34 | 12.34 |
| 23 | 13.5 | 1.9 | 14.1 | 11.6 | 5.0 | 4.9 | 4.56 | 7.34 | 12.34 |
| 24 | 13.5 | 1.8 | 13.3 | 11.7 | 5.0 | 4.9 | 4.56 | 7.34 | 12.34 |
| 25 | 13.5 | 1.7 | 12.8 | 11.6 | 5.0 | 4.9 | 4.56 | 7.34 | 12.34 |
| 26 | 13.3 | 2.0 | 15.0 | 11.3 | 5.0 | 4.9 | 4.56 | 7.34 | 12.34 |
| 21 | 13.1 | 1.7 | 13.0 | 11.4 | 5.0 | 4.9 | 4.56 | 7.34 | 12.34 |
| 33 | 13.1 | 1.6 | 12.2 | 11.5 | 5.0 | 4.9 | 4.56 | 7.34 | 12.34 |

| NCF No. | Filter input (g) | Mass balance (%) | Filtrate yield (%) | Cake yield (%) | Cake THFI (%) | Solids in feed (%) | Filtration Temp ( C) | Filtration Pressure (psig) | Viscosity @ (m Pas) | Cake# resistivity (m/kg) (x 10^10) | Total flow after 30 min (kg/m2) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 27 | 11.2 | 100 | 34.0 | 66.0 | 5.0 | 3.3 | 290 | 50.0 | 100 | 91 | 16 |
| 23 | 11.2 | 99.5 | 92.0 | 7.5 | 31.6 | 2.4 | 260 | 50.0 | 100 | 12 | 31 |
| 24 | 10.8 | 90.7 | 82.4 | 8.3 | 33.6 | 2.8 | 300 | 50.0 | 30 | 58 | 37 |
| 25 | 9.9 | 98.0 | 90.9 | 8.0 | 62.2 | 5.0 | 285 | 50.0 | 20 | 23 | 71 |
| 26 | 9.9 | 99.0 | 90.6 | 8.4 | 47.4 | 4.0 | 295 | 50.0 | 20 | 20 | 77 |
| 21 | 8.6 | 98.3 | 88.4 | 9.9 | 74.0 | 7.3 | 265 | 12.0 | 45 | 2 | 77 |
| 33 | 9.6 | 99.0 | 92.7 | 6.3 | 80.0 | 5.0 | 280 | 50.0 | 25 | 7 | 113 |

| NCF No. | Filter cake analysis | | | | $SO_3$ in ash (%) | ash enrich. factor | ash enrich. factor ($SO_3$-free basis) | coal conversion (1) from THFI | | coal conversion (2) from ash enrichment | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $H_2O$ (%) | ash (%) | ash* (%) | VM (%) | | | | (% daf) | (% daf) | (% daf) | (% daf) |
| 27 | 1.19 | 46.3 | 46.3 | n/m | n/m | 0.34 | 0.34 | 98.9 | 98.9 | 95.2 | 95.2 |
| 23 | 1.77 | 50.7 | 49.8 | n/m | 1.7 | 2.33 | 2.29 | 101 | 101 | 93.6 | 93.5 |
| 24 | 1.94 | 52.3 | 51.2 | n/m | 2.0 | 2.55 | 2.50 | 100 | 100 | 94.1 | 93.9 |
| 25 | 0.98 | 54.4 | 54.4 | n/m | n/m | 4.92 | 4.92 | 94.7 | 94.7 | 94.0 | 94.0 |
| 26 | 2.36 | 51.7 | 51.7 | n/m | n/m | 3.56 | 3.56 | 97.5 | 97.5 | 93.8 | 93.8 |
| 21 | 0.55 | 52.4 | 52.4 | n/m | n/m | 5.63 | 5.63 | 89.1 | 89.1 | 93.4 | 93.4 |
| 33 | 1.35 | 50.0 | 50.0 | n/m | n/m | 5.82 | 5.82 | 94.7 | 94.7 | 92.9 | 92.9 |

* SO3 free basis  n/m = not measured  @ from softening point  # constant rate data

(1) coal conversion = 100 - %solids x (dried digest wt - ash) / (daf coal)
(2) coal conversion = 100 - [{%cake insol - %(cake H2O + ash)} x 100 / (ash enrich)x(100 - coal ash))}

## TABLE 36

## ASH PRECURSORS IN FILTRATE

| Run No | Decant Temp (°C) | Fraction | NCF Run | Filtrate (a) 566°C+ (%) | Filtrate (a) Ash (%) | Ash (%) | % of Dry Coal | % of Dry Coal |
|---|---|---|---|---|---|---|---|---|
| 8ab-LA | 250 | Lights | 28/32 | 38 | 0.07 | 0.18 | 22.6 | 0.04 |
| | | Heavies | 37 | 44 | 1.20 | 2.73 | 18.3 | 0.50 |
| | | Total | | | | | 40.9 | 0.54 |
| 8c-LA | 65 | Lights | - | 24 | 0.02 | 0.08 | 6.1 | 0.005 |
| | | Heavies | 41/42 | 34 | 0.79 | 2.32 | 40.2 | 0.934 |
| | | Total | | | | | 46.3 | 0.94 |
| 9a-LA | NA | Total | 43 | 100 | 1.7 | 1.7 | 42 | 0.71 |

(a) Concentrated by vacuum distillation

## TABLE 37

## YIELDS OF SOLUBLE MATERIAL (566°C+ and 482°C+)

| Run No. | 566°C+ % Dry Coal | | 482°C+ % Dry Coal | |
|---|---|---|---|---|
| | Gross (a) | Net (b) | Gross (a) | Net (b) |
| | Glenharold Lignite | | | |
| 8c-LA Heavies | | | | |
| NCF 34 | 36.3 | 36.3 | 48.2 | 36.0 |
| NCF 36 (c) | 46.3 | 44.7 | 97.5 | 44.3 |
| NCF 39 (c) | 42.4 | 41.4 | 83.0 | 43.6 |
| NCF 40 | 39.3 | 38.6 | 70.1 | 39.7 |
| NCF 41 | 41.1 | 40.6 | 66.3 | 40.4 |
| Mean | | 40.3 | | 40.8 |
| 8c-LA Lights | 6.1 | 6.1 | 61.8 | 11.4 |
| 8c-LA Total | | 46.4 | | 52.2 |
| 9a-LA | | | | |
| NCF 43 | 42 | 42 | 49 | 46 |
| | Ohio Bituminous Coal | | | |
| (129B) | | | | |
| NCF 24 | 71.4 | 71.4 | 111.4 | 73.4 |
| (130B) | | | | |
| NCF 26 | 73.8 | 73.8 | 110.4 | 72.4 |
| Mean | | 72.6 | | 72.9 |

(a) Gross = Total 482 °C+ and 566 °C+ material in filtrate
(b) Net = Gross - 482 °C+ material in solvent/diluent and Gross - 566 °C+ material in solvent/diluent
(c) Aromatic coal-derived diluent used to solubilize first-stage product for filtration. 482°C x 566 °C fraction of diluent greater than amount present in first-stage solvent.

TABLE 38

SIMULATED DISTILLATIONS (AROMATIC CORRECTION) AND SOFTENING POINTS

| Sample | | 488°C+ (%) | 566°C+ (%) | Softening Point (°C) |
|---|---|---|---|---|
| Code | Type* | | | |
| Wilsonville | S | 26 | 0 | |
| Lummus | S | 2 | 0 | |
| Coal Tar | S | 25 | 1 | |
| NCF 2 | F | 40 | 25 | |
| NCF 4 | F | 40 | 18 | |
| NCF 5 | F | 40 | 17 | |
| NCF 12 | F | 45 | 21 | |
| NCF 18 | F | 55 | 33 | |
| | FDR | 84 | 61 | |
| | FDR | 87 | 63 | |
| NCF 20 | FDR2 | 97 | 85 | 285 |
| NCF 24 | F1 | 63 | 50 | 172 |
| | F2 | 64 | 50 | 180 |
| | F3 | 42 | 16 | |
| NCF 26 | F1 | 64 | 51 | 164 |
| | F2 | 48 | 24 | |
| NCF 28 | FDR | 78 | 42 | |
| NCF 32 | FDR | 77 | 40 | |
| NCF 33 | F1 | 33 | 0 | |
| | F2 | | | 159 |
| NCF 34 | F | 60 | 45 | 210 |
| NCF 35 | F | 65 | 52 | 240 |
| NCF 36 | F | 40 | 19 | |
| NCF 37 | F | 40 | 10 | |
| | FDR | 88 | 44 | 130 |
| | FCTHFS | 40 | 9 | |
| | FD | 20 | 0 | |
| NCF 39 | F | 45 | 23 | |
| NCF 40 | F | 50 | 28 | |
| NCF 41 | F | 50 | 31 | |
| NCF 42 | F1 | 52 | 37 | 105 |
| | F2 | 32 | 7 | |
| | FCD | 10 | 0 | |
| NCF 43 | F3 | 29 | 25 | |
| | F3DR | 100 | 99 | ~320 |
| | F3D | 2 | 0 | |
| | FCD | 4 | 0 | |
| 8LA A+B | Lights | 46 | 19 | |
| | LDR | 49 | 27 | |
| 8LA C | Lights | 30 | 3 | |
| | LDR | 80 | 24 | |

Type*

| | |
|---|---|
| S | Solvent or Diluent |
| F | Filtrate |
| FDR | Distillation Residue (Concentrated Filtrate for Upgrading) |
| FCTHFS | THF Solubles from Filter Cake |
| FD | Distillate from Filtrate |
| FCD | Distillate from Filter Cake |
| Lights | Decanted Liquid |
| LDR | Concentrated Decanted Liquid |

TABLE 39

PHYSICOCHEMICAL PROPERTIES OF AKZO AO-60 CATALYST

| | |
|---|---|
| Nominal size | 1/16" |
| wt % Mo | 12.25 |
| wt % Ni | 2.6 |
| Bulk density, g/cc | 0.57 |
| Surface area, $m^2/g$ | 286 |

TABLE 40

RESULTS OF SCREENING TESTS OF CATALYST PRECURSORS IN DEASHED RESID

| Run no. | feedstock avg (2) | R5-290-1 | R5-292-1 | R5-320-2 | R5-307-2 | R5-318-2 | R5-314-1 | R5-318-1 R5-334-1 | R5-320-1 |
|---|---|---|---|---|---|---|---|---|---|
| Catalyst precursor | none | none | Molyvan L | Molyvan L | Mo naph-thenate | Mo naph-thenate | AO-60 | AO-60 | AO-60 sulfided ex situ |
| Pretreat time @ °C | - | none | none | 30 @ 375 | none | 30 @ 375 | none | 30 @ 375 | none |
| Reaction time @ °C | - | 60 @ 440 | 60 @ 440 | 60 @ 440 | 60 @ 440 | 60 @ 440 | 60 @ 440 | 60 @ 440 | 60 @ 440 |
| Ni, ppmw feed | - | - | - | - | - | - | 173 | 171 | 175 |
| Mo, ppmw feed | - | - | 998 | 988 | 997 | 1010 | 817 | 803 | 825 |
| Products, wt % maf feed | | | | | | | | | |
| Hydrocarbon gas, $C_1$-$C_6$+ | - | 6.2 | 5.8 | 6.2 | 9.4 | 6.0 | 9.4 | 7.2 | 5.7 |
| CO + $CO_2$ | - | 0.3 | 0.0 | 0.4 | 0.9 | 0.2 | 1.1 | 0.3 | 0.1 |
| 566 °C- | 24.3 | 32.3 | 45.0 | 45.2 | 42.2 | 45.7 | 41.0 | 51.0 | 47.5 |
| 566 °C+ | 75.7 | 61.2 | 49.2 | 48.2 | 47.5 | 48.1 | 48.5 | 41.5 | 46.7 |
| Total | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Derived values | | | | | | | | | |
| Resid conversion, wt % 566 °C+ | - | 19.2 | 35.1 | 36.3 | 37.3 | 36.5 | 36.0 | 45.2 | 38.4 |
| $H_2$ consumed, mg/g maf feed | - | 7 | 18 | 18 | 17 | 16 | 19 | 18 | 16 |
| Material balance index | 99 (avg.) | 97 | 97 | 93 | 96 | 97 | 103 | 86 | 95 |

TABLE 41

ELEMENTAL BALANCES FOR CATALYST SCREENING TESTS

| Run no. | wt % | | | | | |
|---|---|---|---|---|---|---|
| | C | H | N | S | O | Ash |
| R5-307-2 | 97.2 | 98.5 | 100.0 | 76.4 | 100.0 | 452.9 |
| R5-314-1 | 105.2 | 99.2 | 100.0 | 87.4 | 100.0 | 58.7 |
| R5-318-1 | 86.7 | 94.4 | 100.0 | 90.8 | 100.0 | 71.0 |
| R5-318-2 | 99.0 | 98.0 | 100.0 | 100.4 | 100.0 | 95.7 |
| R5-320-1 | 101.4 | 99.0 | 100.0 | 96.9 | 100.0 | 62.5 |
| R5-320-2 | 95.5 | 97.0 | 100.0 | 104.1 | 100.0 | 86.3 |
| Average | 97.5 | 97.7 | 100.0 | 92.7 | 100.0 | 137.8 |

TABLE 42

RESULTS OF 5 AND 30 MINUTE PRETREATMENT TESTS WITH WILSONVILLE RUN 258A DEASHED RESID (a)

| Run no. | R5-290-1 | R5-292-1<br>R6-51-2 | R6-79-1<br>R6-37-1 | R6-32-1<br>R6-44-2 | R6-36-1<br>R6-44-1 | R6-36-2<br>R6-72-1 | R6-32-2<br>R6-39-1 | R5-320-2<br>R6-46-1 | R6-60-1<br>R6-65-1 |
|---|---|---|---|---|---|---|---|---|---|
| Catalyst precursor | none | Molyvan L | Molyvan L | Molyvan L | Molyvan L | Molyvan L | Molyvan L | Molyvan L | Molyvan L |
| Pretreat time @ °C | none | none | 5@300 | 5@340 | 5@375 | 30@300 | 30@340 | 30@375 | 30@440 |
| Mo, ppmw feed | - | 1013 | 1074 | 1041 | 1013 | 1078 | 1093 | 1020 | 1059 |
| Products, wt % MAF feed | | | | | | | | | |
| Hydrocarbon gas, $C_1$-$C_6$+ | 6.2 | 6.0 | 5.8 | 6.6 | 5.8 | 6.3 | 5.8 | 6.4 | 8.8 |
| CO + $CO_2$ | 0.3 | 0.1 | 0.1 | 0.2 | 0.0 | 0.2 | 0.0 | 0.2 | 0.2 |
| 566 °C- | 32.3 | 43.6 | 41.2 | 39.6 | 42.0 | 40.0 | 38.5 | 42.2 | 44.6 |
| 566 °C+ | 61.2 | 50.3 | 52.9 | 53.6 | 52.2 | 53.5 | 55.7 | 51.2 | 46.4 |
| Total | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Derived values | | | | | | | | | |
| Resid conversion, wt % 566 °C+ | 19.2 | 33.6 | 30.2 | 29.2 | 31.1 | 29.4 | 26.5 | 32.4 | 38.8 |
| $H_2$ consumed, mg/ g maf feed | 7 | 22 | 16 | 22 | 19 | 18 | 19 | 20 | 24 |
| Material balance index | 97 | 95 | 92 | 94 | 92 | 95 | 92 | 93 | 92 |

a. Pretreatment times are shown, followed by hydrotreating at 440 °C for 60 minutes. 3 g R-258A deashed resid used as feedstock, with 1000 ppmw Mo in Molyvan L (1:1 in hexadecane, total feed basis) used as the catalyst precursor. 2% $H_2S$ in hydrogen was added to sulfide the catalyst, 10.1 MPa (1450 psig) total pressure (cold).

TABLE 43

RESULTS OF 30-MINUTE PRETREATMENT STUDIES WITH
WILSONVILLE RUN 258A DEASHED RESID (a)

| Run No. | R6-40-1<br>R6-53-1 | R6-183-1<br>R6-199-1 | R6-267-1<br>R6-267-2 | R6-57-1<br>R6-57-2 |
|---|---|---|---|---|
| Catalyst precursor | Molyvan L | Molyvan L | Molyvan L | Molyvan L |
| Pretreat time @°C | none | 30 @ 300 | 30 @ 340 | 30 @375 |
| Mo, ppmw feed | 1078 | 994 | 997 | 1028 |
| Products, wt % MAF feed | | | | |
| Hydrocarbon gas, $C_1$-$C_6$+ | 3.7 | 2.3 | 1.7 | 4.0 |
| CO + $CO_2$ | 0.2 | 1.1 | 0.9 | 0.2 |
| 566°C- | 37.5 | 40.0 | 38.7 | 36.6 |
| 566°C+ | 58.6 | 56.6 | 58.7 | 59.2 |
| Total | 100 | 100 | 100 | 100 |
| Derived values | | | | |
| Resid conversion, wt % 566°C+ | 22.6 | 25.3 | 22.5 | 21.8 |
| $H_2$ consumed, mg/ g maf feed | 11 | 14 | 11 | 9 |
| Material balance index | 95 | 96 | 96 | 96 |

(a) Pretreatment times are shown, followed by hydrotreating at 440°C for 30 minutes. 3 g R-258A deashed resid used as feedstock, with 1000 ppmw Mo in Molyvan L (1:1 in hexadecane, total feed basis) used as the catalyst precursor. 2% $H_2S$ in hydrogen was added to sulfide the catalyst, 10.1 MPa (1450 psig) total pressure (cold).

TABLE 44

FIRST-STAGE PRODUCT CATALYTIC UPGRADING TESTS
60-MINUTE RUNS

| Composited Filtrate | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Sample No. | Rxn. Temp, °C | Mo conc., log ppm | H/C & COx Gas Yield, wt % MAF feed | 566°C-, wt %MAF feed | 566°C+ resid, wt % MAF feed | H2 Consumed, mg/g MAF Feed | Resid Conv., wt % MAF Resid | Ultimate distillate (MA No.) | Ultimate resid (MA No.) |
| Blank Filtrate R6-79-3 | - | - | - | 71.6 | 28.4 | - | - | NO | No sample |
| IN-HOUSE distillation | - | - | - | 27.9 | 72.1(calc) | - | - | 43382 | |
| Blank Filtrate R6-100-3 | - | - | - | 17.0* | 83.0* | - | - | 43413 | 43412 |
| R6-94-1 | 400 | 3 | 4.1<br>0.7 | 27.1 | 68.1 | 20 | 6 | 43376 | 43375 |
| R6-93-2 | 400 | 4 | 4.8<br>0.5 | 33.7 | 61.0 | 25 | 15 | 43374 | 43373 |
| R6-95-1 | 440 | 3 | 10.1<br>0.9 | 46.4 | 42.7 | 33 | 41 | 43378 | 43377 |
| R6-93-1 | 440 | 4 | 11.4<br>0.6 | 54.1 | 33.9 | 40 | 53 | 43372 | 43371 |
| Molyvan L- AR | - | - | - | - | - | - | - | 43383 | |

* Distillate yield for Run R6-100-3 was restated basedon SIMDIS results. A different distillation curve was obtained for this sample, compared to the "In-house distillation" full range material.

TABLE 45

FIRST-STAGE PRODUCT CATALYTIC UPGRADING TESTS
60-MINUTE RUNS

| Deashed Resid | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Sample No. | Reaction Temp, °C | Mo conc., log ppm | H/C & COx Gas Yield, wt % MAF feed | 566°C-, wt % MAF feed | 566°C+ resid, wt % MAF feed | $H_2$ Consumed, mg/g MAF Feed | Resid Conv., wt % MAF Resid | Ultimate distillate (MA No.) | Ultimate resid (MA No.) |
| blank deashed resid R6-51-1 | - | - | - | 27.2 | 72.8 | - | - | 43177 | 43178 |
| R5-339-1 (alt. R6-92-1) | 400 | 3 | 0.80 | 36.2 | 63.0 | 8 | 17 | 43406 | 43405 |
| R6-95-3 | 400 | 4 | 1.70 | 25.3* | 73.0* | 19 | 4* | 43380 | 43379 |
| R6-51-2 (alt.R5-292-1) | 440 | 3 | 6.20.1 | 42.3 | 51.4 | 25 | 32 | 43408 | 43407 |
| R6-99-1 | 440 | 4 | 6.60.1 | 38.3* | 55.0* | 23 | 27* | 43411 | 43410 |
| R6-106-1 (duplicate of R6-99-1) | 440 | 4 | 7.10.1 | 43.3* | 49.5* | 40 | 35* | - | - |

*Distillate yields for Runs R6-95-3, R6-99-1 and R6-106-1 were restated based on SIMDIST results.

TABLE 46

FIRST-STAGE PRODUCT CATALYTIC UPGRADING TESTS
LOW-TEMPERATURE, 60-MINUTE RUNS

| Deashed Resid | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Sample No. | Reaction Temp, °C | Mo conc., log ppm | H/C & COx Gas Yield, wt % MAF feed | 566°C⁻, wt % MAF feed | 566°C⁺ resid, wt % MAF feed | $H_2$ Consumed, mg/g MAF Feed | Resid Conv., wt % MAF Resid | SIMDIST Correction to Conversion |
| R5-339-1 (alt. R6-92-1) | 400 | 3 | 0.8<br>0 | 36.2 | 63.0 | 8 | 17 | - |
| R6-92-1 | 400 | 3 | 1.4<br>0.1 | 28.5 | 70.0 | 7 | 8 | +12 |
| R6-92-2 | 420 | 3 | 2.8<br>0.1 | 37.9 | 59.2 | 11 | 22 | +13 |
| R6-99-2 | 420 | 3 | 2.8<br>0.1 | 35.4 | 61.7 | 11 | 19 | +14 |
| R6-100-2 (50/50 deashed resid and 488°C- distillate) | 420 | 4 | 9.8<br>0.3 | 25.8 | 64.2 | 20 | 15 | +18 |
| R6-19-1 (50/50 deashed resid and 488°C- distillate) | 440 | 4 | 10.0<br>0.3 | 50.2 | 39.5 | 23 | 48 | - |

TABLE 47

COMPARISON OF CATALYTIC UPGRADING TEST RESULTS (a)

| CONSOL Sample no. | Coal source | Digest solvent @ temp & time | Filtration and hydrotreat run no. | 566°C+ to hydrotreater, wt % MAF feed | 566°C+ resid conversion, wt % MAF resid | $C_1$-$C_3$ gas yield, wt % feed | $C_1$-$C_3$ gas yield per g resid converted | $H_2$ uptake, mg/g MAF feed | $H_2$ uptake per g resid converted |
|---|---|---|---|---|---|---|---|---|---|
| Wilsonville Run258A DAR | Black Thunder subbit | n/a | R6-106-1 | 75.7 | 35 | 4.4 | 16.6 | 40 | 151 |
| Composite d Filtrate | Black Thunder subbit | various 350-400°C | R6-93-1 | 72.1 | 53 | 8.5 | 22.2 | 40 | 105 |
| DAR & 488°C-distillate | Black Thunder subbit | n/a | R6-19-1 | 37.8 | 48 | 4.1 | 22.4 | 12 | 66 |
| Run 5-LA | Black Thunder subbit | 488°C-dist. at 350°C | NCF18-R R6-120-1 | 60.7 | 66 | 7.7 | 19.2 | 38 | 95 |
| Run 5-LA | Black Thunder subbit | 488°C-dist. at 350°C | NCF18-2R R6-117-1 | 62.7 | 63 | 8.1 | 20.4 | 39 | 99 |
| Run 7-LA | Freedom Mine lignite | 350°C for 60 min | NCF22 R6-162-1 | 59.8 | 77 | 7.2 | 15.7 | 38 | 83 |
| Runs 8a-LA and 8b-LA (8ab-LA) | Glenharold lignite | 488°C-dist. at 350°C for 60 min | NCF28..32 R6-207-3 | 38.3 | 71 | 5.5 | 20.3 | 26 | 96 |
| 8ab-LA concentrat e | Glenharold lignite | 488°C-dist. at 350°C | NCF28..32 R6-240-2 | 66.8 | 64 | 7.7 | 18.0 | 39 | 91 |
| Run 9a-LA | Glenharold lignite | Lummus | NCF43-F2DR R6-261-1 | 99.7 | 67 | 8.3 | 12.4 | 49 | 73 |
| 121 A | KY/OH mine bituminous | 488°C-dist. at 400°C | NCF21-FR R6-156-1 | 72.2 | 57 | 7.7 | 18.6 | 38 | 92 |

a. Hydrotreated at 440°C for 60 min with 10,000 ppm Mo in Molyvan L.

TABLE 48

HIGH/LOW PARAMETRIC STUDY VALUES

| Factor | Low value | High value |
|---|---|---|
| Time, minutes | 30 | 60 |
| Temperature, °C | 400 | 440 |
| Mo concentration, ppmw (total solid feed basis) | 1000 | 10,000 |

TABLE 49

DEPENDENT VARIABLES EVALUATED

| Effect | Units | $R^2$ |
|---|---|---|
| % Rc | 1050 °F$^+$ resid conversion | 0.972 |
| $C_1$-$C_3$ Gas | Methane - propane gas yield, wt % MAF filtrate | 0.984 |
| $C_4$+ Gas | Butane plus gas yield, wt % MAF filtrate | 0.617 |
| CO+$CO_2$ | CO and $CO_2$ gas yield, wt % MAF filtrate | 0.535 |
| TGas | Total gas yield, wt % MAF filtrate | 0.915 |
| mg $H_2$ | $H_2$ consumption, mg/g MAF filtrate | 0.816 |

TABLE 50

SUMMARY OF ESTIMATED COEFFICIENTS (a)

| | Inter-cept | t (b) Coeff (P) | T (b) Coeff (P) | Mo (b) Coeff (P) | txT (b) Coeff (P) | txMo (b) Coeff | TxMo (b) Coeff |
|---|---|---|---|---|---|---|---|
| % Rc | 48.41 | 7.86 (.0001) | 13.73 (.0001) | 2.23 (.0195) | - | - | - |
| $C_1$-$C_3$ Gas | 2.94 | 0.50 (.0001) | 1.37 (.0001) | 0.19 (.0097) | 0.29 (.0007) | - | - |
| $C_4^+$ Gas | 1.51 | 0.19 (.2916) | 0.34 (.0704) | 0.47 (.0192) | 0.24 (.1840) | - | - |
| CO+$CO_2$ | 0.33 | 0.01 (.6051) | 0.07 (.0062) | 0.01 (.7294) | - | - | - |
| TGas | 4.78 | 0.69 (.0064) | 1.78 (.0001) | 0.67 (.0080) | 0.53 (.0261) | - | - |
| mg $H_2$ | 17.80 | 2.76 (.0028) | 3.70 (.0003) | 1.97 (.0197) | - | - | - |

a. All three way interaction coefficients (txTxMo) are small and set equal to zero. Coefficient estimates are for coded variables (-1,0,+1).

b. t = time, minutes; T = temperature, °C; Mo = ppmw Mo in Molyvan L on filtrate feed; txT = two-way interaction of time with temperature; txMo

TABLE 51

PARAMETRIC CATALYTIC UPGRADING STUDY

| Run Number | R6-205-1 | R6-205-2 | R6-205-3 | R6-207-1 | R6-207-2 | R6-207-3 | R6-211-1 | R6-211-2 |
|---|---|---|---|---|---|---|---|---|
| Run Order No./ Block Number/ Standard Order No. | 1/1/4 | 2/1/2 | 3/1/1 | 4/1/6 | 5/1/5 | 6/1/8 | 7/1/3 | 8/1/7 |
| Reaction temp., °C | 440 | 400 | 400 | 400 | 400 | 440 | 440 | 440 |
| Run time, min | 60 | 60 | 30 | 60 | 30 | 60 | 30 | 30 |
| Fresh Mo, ppm feed | 994 | 1,020 | 1,010 | 9,970 | 9,990 | 9,960 | 991 | 10,090 |
| Products, wt % MAF feed | | | | | | | | |
| Hydrocarbon gas, $C_1$-$C_3$ | 4.4 | 1.6 | 1.1 | 2.1 | 1.6 | 5.5 | 3.4 | 3.7 |
| Hydrocarbon gas, $C_4$+ | 1.5 | 0.6 | 1.1 | 2.5 | 2.5 | 3.1 | 0.8 | 1.2 |
| CO + $CO_2$ | 0.5 | 0.3 | 0.2 | 0.3 | 0.2 | 0.2 | 0.4 | 0.3 |
| 566 °C- | 82.8 | 76.2 | 70.4 | 73.5 | 69.0 | 80.2 | 75.9 | 78.7 |
| 566 °C+ | 10.8 | 21.3 | 27.2 | 21.6 | 26.7 | 11.0 | 19.5 | 16.1 |
| Total | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| Derived values | | | | | | | | |
| Resid conversion, wt % 566 °C+ | 71.8 | 44.5 | 29.1 | 43.7 | 30.3 | 71.3 | 49.0 | 57.9 |
| $H_2$ consumed, mg/ g MAF feed | 20 | 17 | 6 | 18 | 18 | 26 | 17 | 17 |
| Material balance index | 92 | 94 | 98 | 88 | 92 | 81 | 91 | 83 |

TABLE 51 (Continued)

PARAMETRIC CATALYTIC UPGRADING STUDY

| Run Number | R6-211-3 | R6-212-1 | R6-212-2 | R6-212-3 | R6-218-1 | R6-218-2 | R6-219-1 | R6-219-2 |
|---|---|---|---|---|---|---|---|---|
| Run Order No./ Block Number/ Standard Order No. | 9/2/15 | 10/2/13 | 11/2/11 | 12/2/14 | 13/2/9 | 14/2/10 | 15/2/16 | 16/2/12 |
| Reaction temp., °C | 440 | 400 | 440 | 400 | 400 | 400 | 440 | 440 |
| Run time, min | 30 | 30 | 30 | 60 | 30 | 60 | 60 | 60 |
| Fresh Mo, ppm feed | 10,050 | 9,980 | 998 | 10,030 | 992 | 976 | 9,980 | 1,030 |
| Products, wt % MAF feed | | | | | | | | |
| Hydrocarbon gas, $C_1$-$C_3$ | 3.6 | 1.4 | 3.4 | 1.6 | 1.3 | 1.7 | 5.4 | 5.1 |
| Hydrocarbon gas, $C_4^+$ | 2.7 | 0.9 | 1.1 | 0.7 | 0.4 | 0.6 | 2.3 | 2.2 |
| CO + $CO_2$ | 0.5 | 0.3 | 0.4 | 0.3 | 0.2 | 0.2 | 0.5 | 0.4 |
| 566 °C$^-$ | 77.1 | 68.6 | 75.8 | 76.6 | 69.7 | 72.1 | 81.6 | 79.3 |
| 566 °C$^+$ | 16.1 | 28.8 | 19.3 | 20.8 | 28.4 | 25.4 | 10.2 | 13.0 |
| Total | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| Derived values | | | | | | | | |
| Resid conversion, wt % 566 °C$^+$ | 57.9 | 24.9 | 49.7 | 45.7 | 25.7 | 33.7 | 73.5 | 66.0 |
| $H_2$ consumed, mg/ g MAF feed | 20 | 15 | 17 | 16 | 10 | 13 | 28 | 27 |
| Material balance index | 85 | 90 | 91 | 87 | 96 | 96 | 79 | 87 |

TABLE 52

ULTIMATE ANALYSES OF DISTILLATE FRACTIONS

| Run Number | Analysis number | C, wt % | H, wt % | N, wt % | O+S + Ash (diff) |
|---|---|---|---|---|---|
| AR (a) NCF 28..32 (Feedstock) | 44015 | 87.65 | 8.09 | 1.64 (d) | 2.62 |
| R6-204-1D (b) (NCF 28..32) | 44016 | 89.21 | 9.29 | 1.74 | -0.24 |
| R6-204-1R (c) (NCF 28..32) | 44017 | 85.17 | 6.39 | 1.47 | 6.97 |
| R6-205-1D | 43945 | 90.86 | 9.41 | 1.54 | -1.81 |
| R6-205-1R | 43946 | 85.84 | 6.95 | 1.47 | 5.74 |
| R6-205-2D | 43947 | 87.12 | 9.82 | 1.44 | 1.62 |
| R6-205-2R | 43948 | 88.01 | 6.10 | 5.33 | 0.56 |
| R6-205-3D | 43949 | 84.23 | 10.03 | 1.35 | 4.39 |
| R6-205-3R | 43950 | 86.12 | 6.81 | 1.41 | 5.66 |
| R6-207-1D | 43998 | 89.83 | 9.27 | 1.63 | -0.73 |
| R6-207-1R | 43999 | 81.34 | 5.83 | 1.70 | 11.13 |
| R6-207-2D | 44000 | 85.05 | 9.55 | 1.79 | 3.61 |
| R6-207-2R | 44001 | 78.78 | 5.43 | 1.78 | 14.01 |
| R6-207-3D | 44002 | 88.71 | 9.26 | 1.93 | 0.10 |
| R6-207-3R | Insufficient sample | - | - | - | - |
| R6-211-1D | 44003 | 88.13 | 9.20 | 1.68 | 0.99 |
| R6-211-1R | 44004 | 88.25 | 4.98 | 2.66 | 4.11 |
| R6-211-2D | 44005 | 85.10 | 9.04 | 1.91 | 3.95 |
| R6-211-2R | Insufficient sample | - | - | - | - |
| R6-211-3D | 44006 | 88.03 | 8.99 | 2.67 | 0.31 |
| R6-211-3R | Insufficient sample | - | - | - | - |
| R6-212-1D | 44007 | 87.69 | 9.16 | 2.23 | 0.92 |
| R6-212-1R | 44008 | 80.27 | 5.47 | 1.53 | 12.73 |
| R6-212-2D | 44099 | 82.76 | 9.82 | 1.64 | 5.78 |
| R6-212-2R | 44100 | 88.89 | 6.10 | 2.13 | 2.88 |
| R6-212-3D | 44101 | 87.38 | 9.47 | 1.53 | 1.62 |
| R6-212-3R | 44102 | 79.31 | 6.13 | 1.25 | 13.31 |
| R6-218-1D | 44103 | 89.94 | 9.42 | 0.99 | -0.35 |
| R6-218-1R | 44104 | 85.79 | 6.57 | 1.51 | 6.13 |
| R6-218-2D | 44105 | 86.75 | 9.34 | 1.57 | 2.34 |
| R6-218-2R | 44106 | 85.41 | 6.56 | 1.43 | 6.60 |
| R6-219-1D | 44117 | 90.32 | 9.21 | 1.47 | -1.00 |
| R6-219-1R | Insufficient sample | - | - | - | - |
| R6-219-2D | 44118 | 89.39 | 8.93 | 1.65 | 0.03 |
| R6-219-2R | Insufficient sample | - | - | - | - |

(a) AR = as received (b) D = distilate (c) R = resid (d) determined from analyses of distillate and resid fractions

TABLE 53

EVALUATION OF MOLYVAN L ACTIVITY IN SIMULATED RECYCLE

| Run no., First pass<br>Second pass | R5-279-1& R5-283-1, feedstock | R6-51-2<br>- | R6-134-1<br>R6-134-2 | R6-74-1<br>R6-88-1 | R6-113-1<br>R6-114-1 |
|---|---|---|---|---|---|
| Reaction temp., First pass<br>Second pass | - | 440<br>- | 440<br>440 | 440<br>440 | 440<br>440 |
| Run time, First pass<br>Second pass | - | 60<br>- | 60<br>60 | 60<br>60 | 60<br>60 |
| Fresh Mo, ppm feed | - | 1029 | - | - | 100 |
| Recycle Mo, ppm feed | - | - | 1006 | 800 | 793 |
| Products, wt % MAF feed | | | | | |
| Hydrocarbon gas, $C_1$-$C_6$+ | - | 6.2 | 4.4 | 4.6 | 5.0 |
| CO + $CO_2$ | - | 0.1 | 0.1 | 0.1 | 0.1 |
| 566 $^oC^-$ | 24.3 | 42.3 | 47.0 | 38.3 | 43.9 |
| 566 $^oC^+$ | 75.7 | 51.4 | 48.5 | 57.0 | 51.0 |
| Total | 100 | 100 | 100 | 100 | 100 |
| Derived values | | | | | |
| Second-pass resid conversion, wt % 566 $^oC^+$ | - | 32.1 | 33.7 | 24.7 | 32.7 |
| $H_2$ consumed, mg/ g MAF feed | - | 25 | 15 | 12 | 14 |
| Material balance index | 98.6 (avg.) | 92.5 | 92.5 | 93.3 | 93.8 |

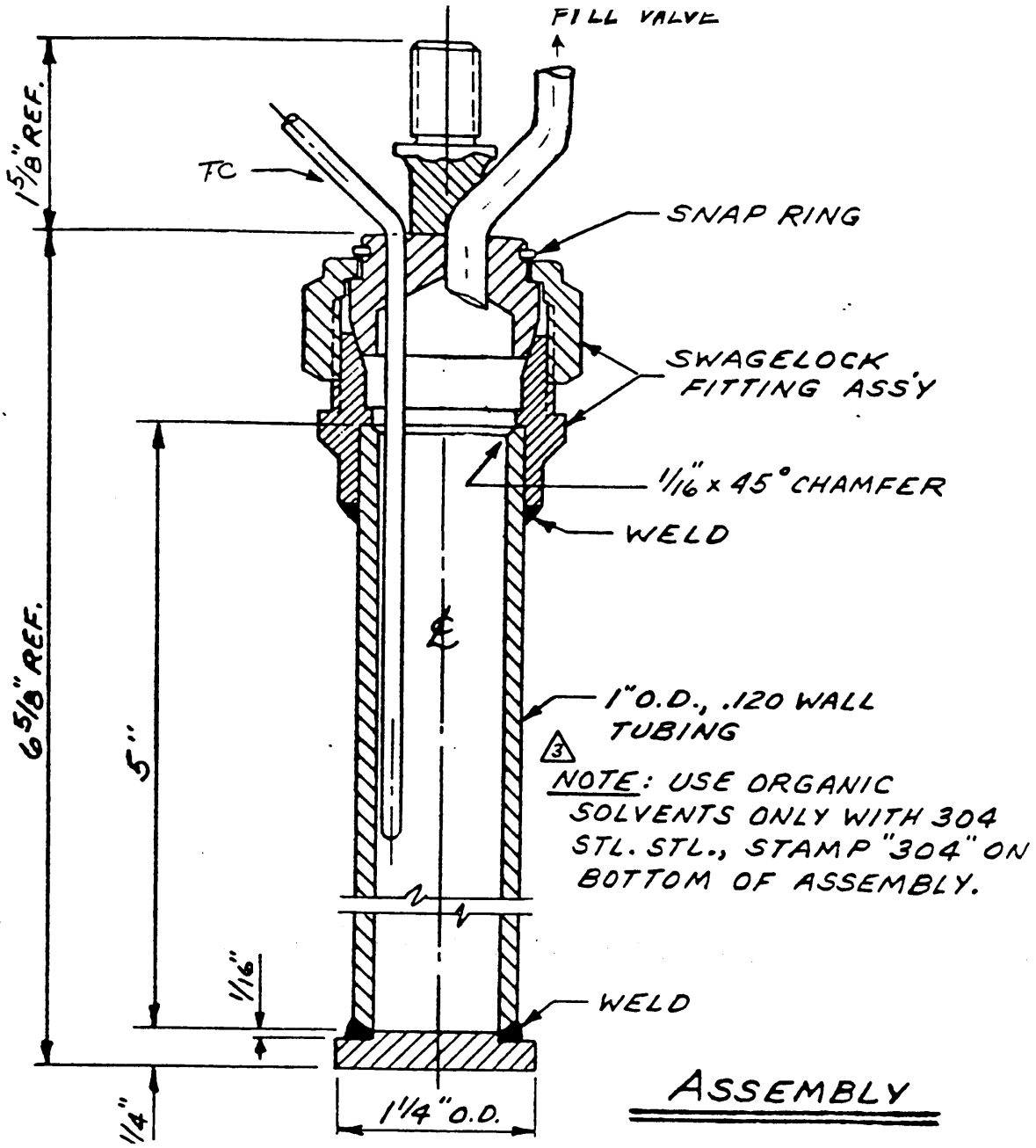



Figure 1. 45 mL Stainless Steel Microautoclave Design Used for First-Stage Coal Solubilization.

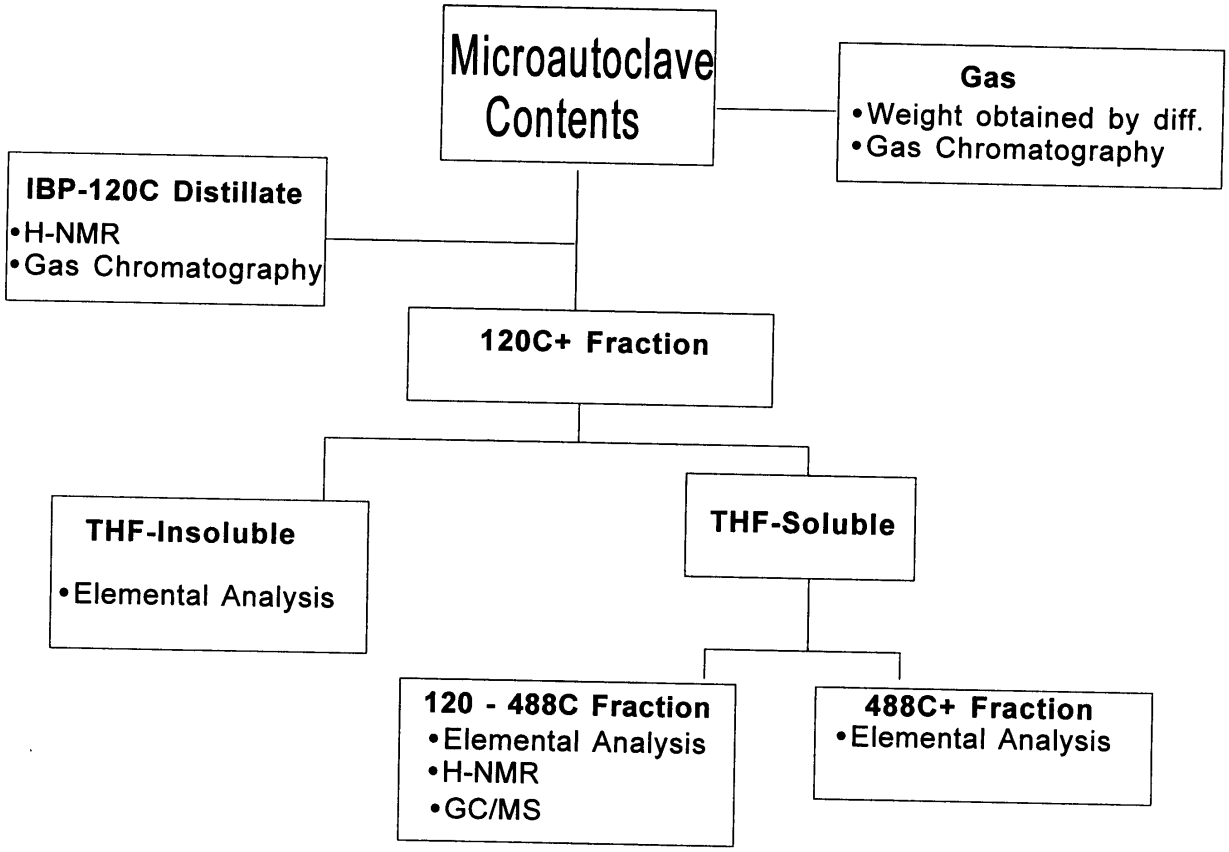



Figure 2. Microautoclave-Scale Product Material Balance and Analyses Scheme.

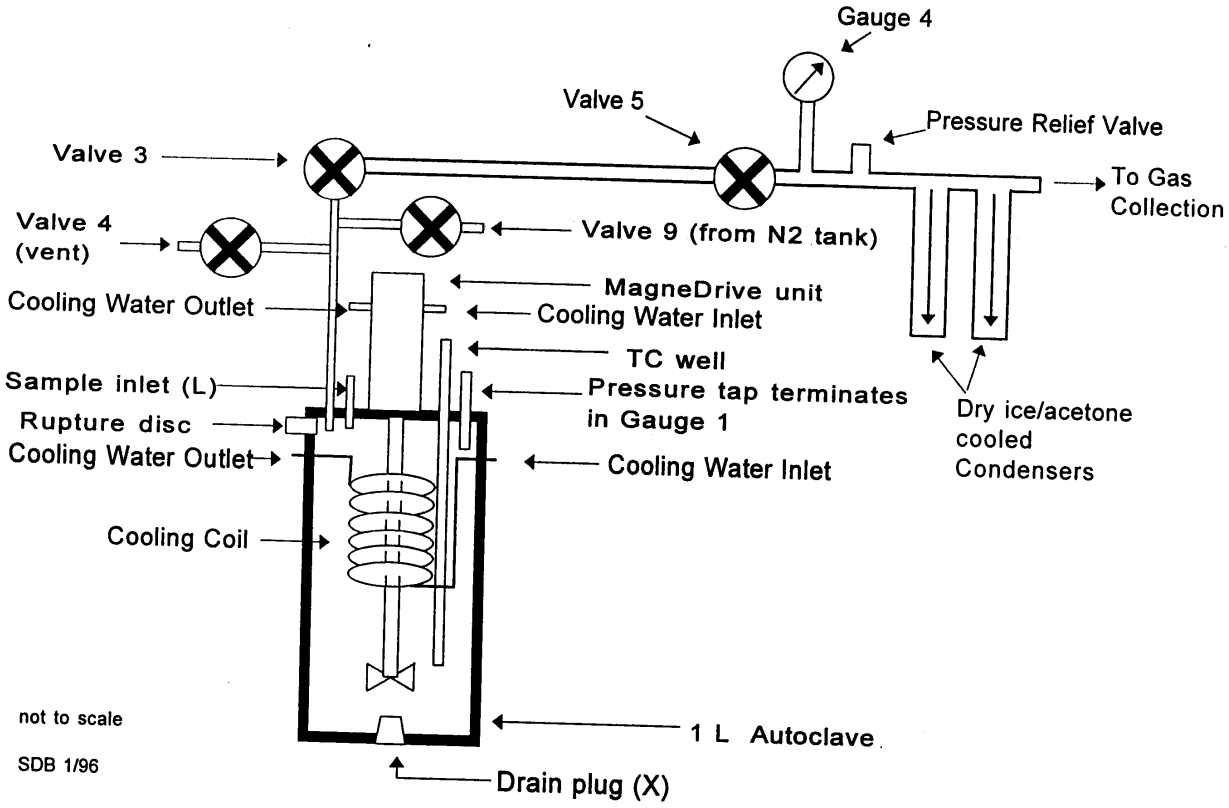



Figure 3. One-Liter Autoclave-Scale Test Configuration 1.

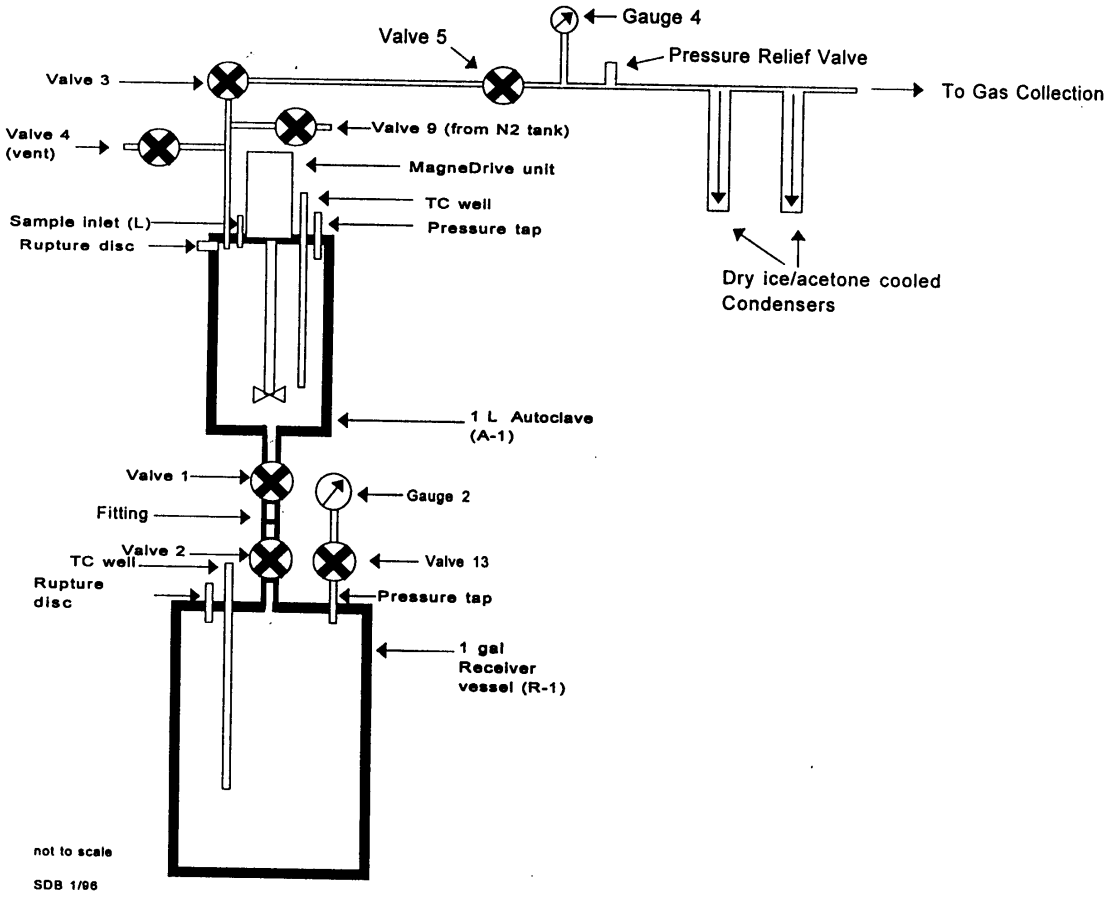



Figure 4. One-Liter Autoclave-Scale Test Configuration 2.

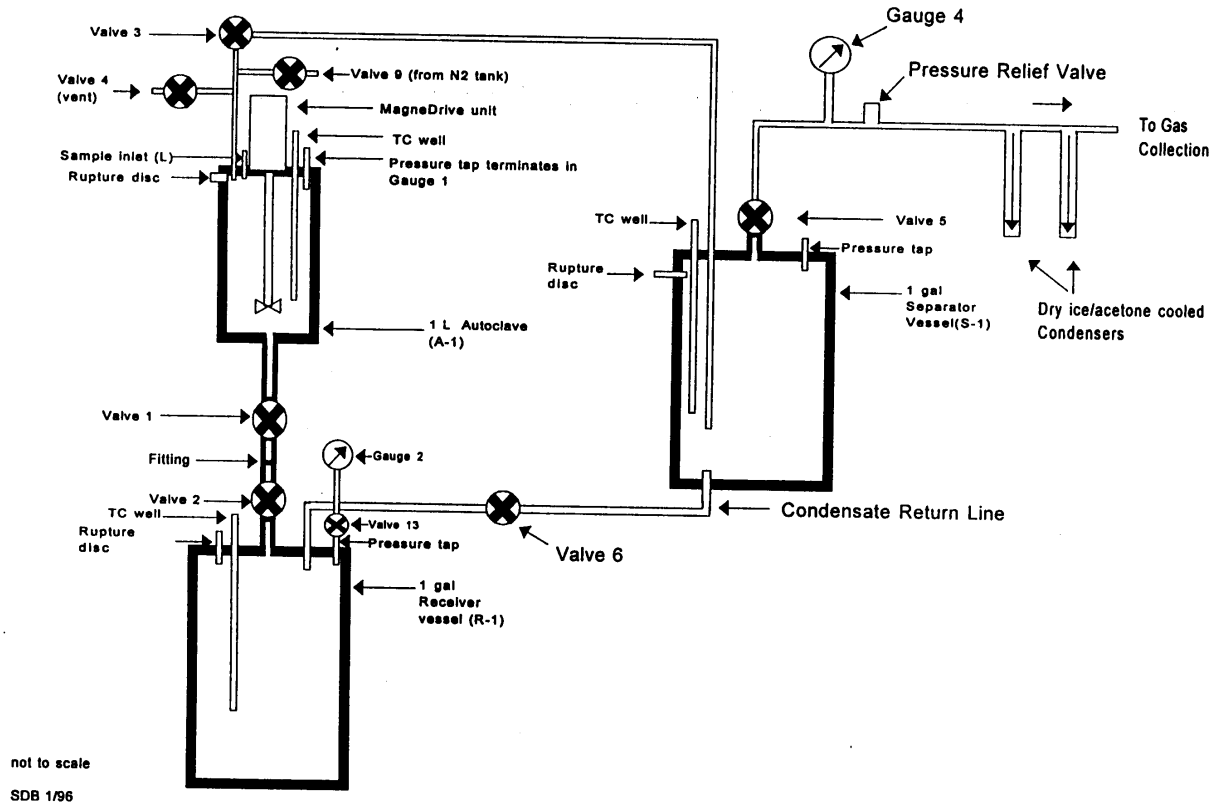



Figure 5. One-Liter Autoclave-Scale Test Configuration 3.

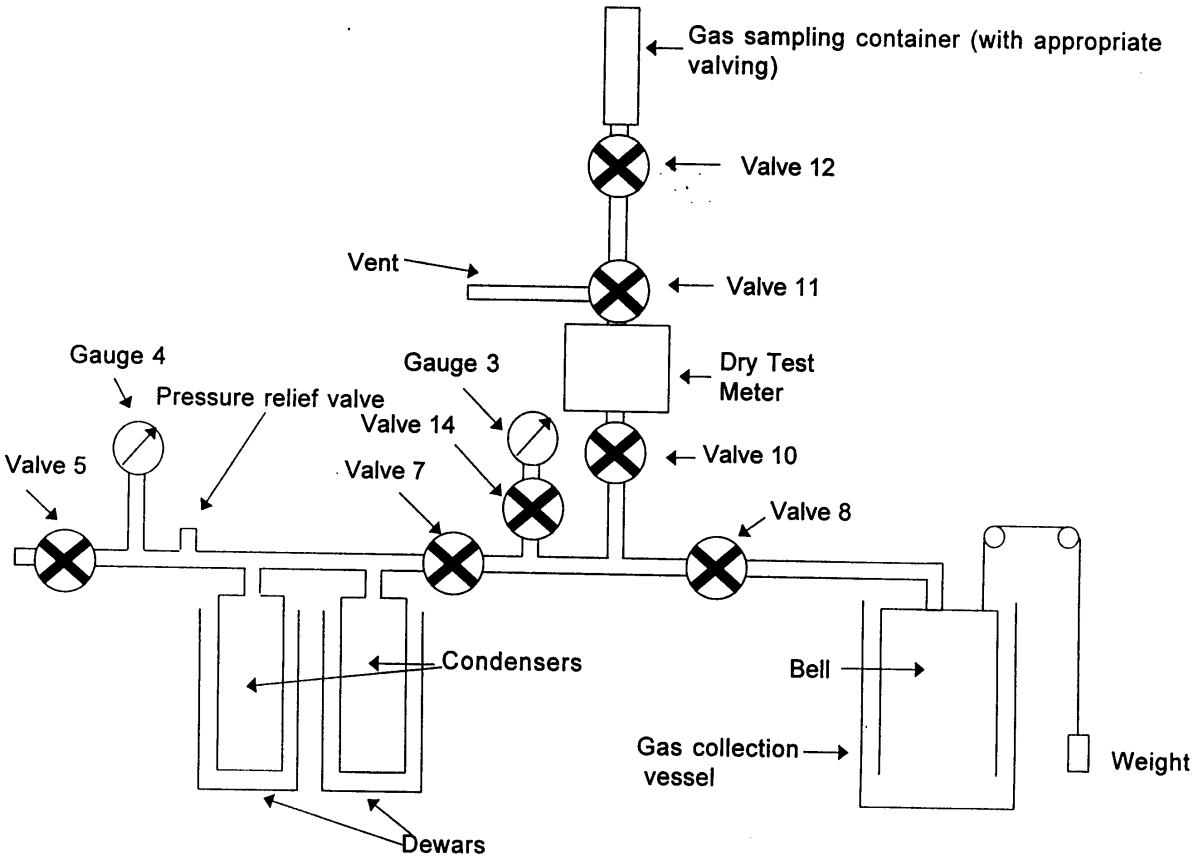



Figure 6. Gas Collection Configuration for One-Liter Autoclave Reaction System.

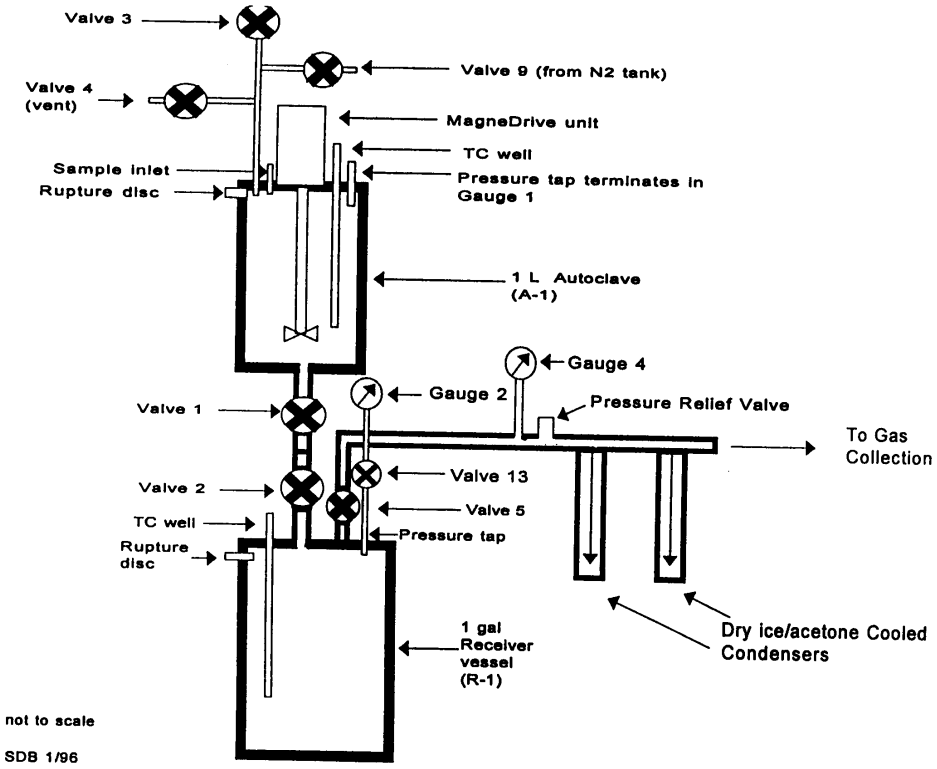



Figure 7. Method 3 Configuration for One-Liter Autoclave Product Collection.

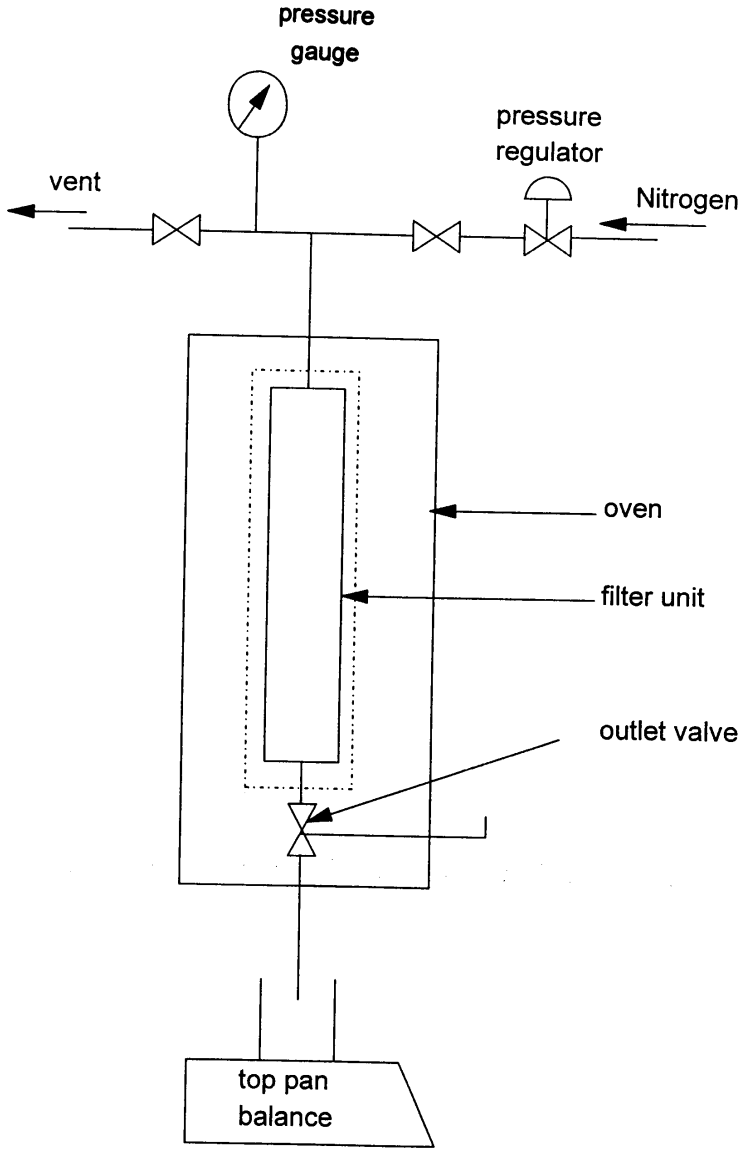



Figure 8. Microfiltration Rig.

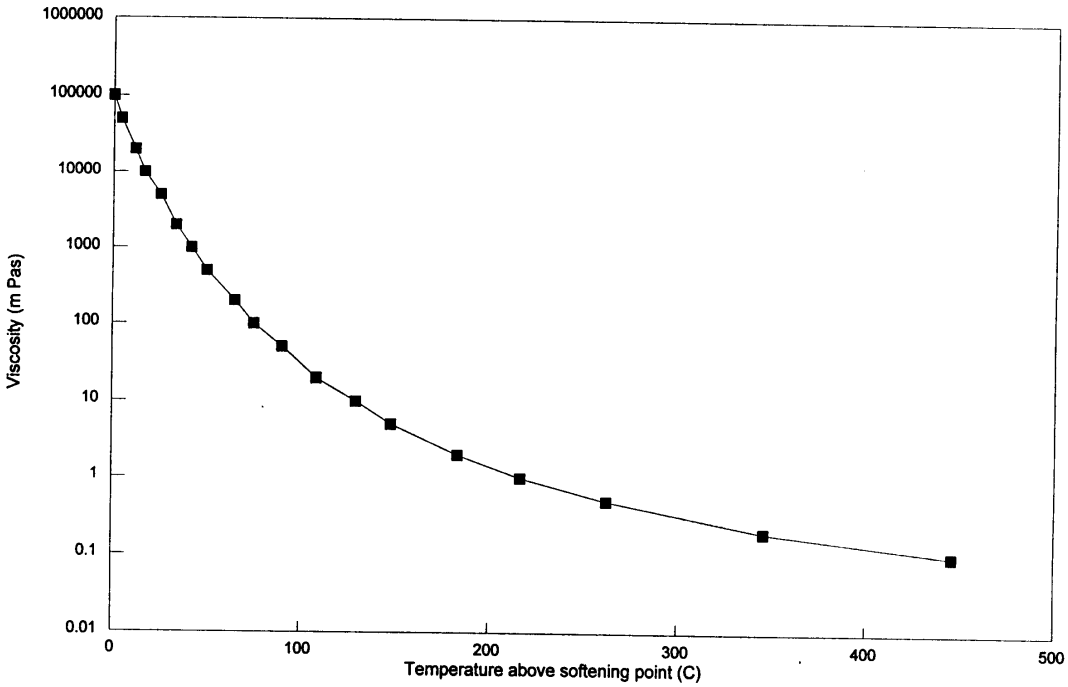



Figure 9. Generalized Viscosity Curve.

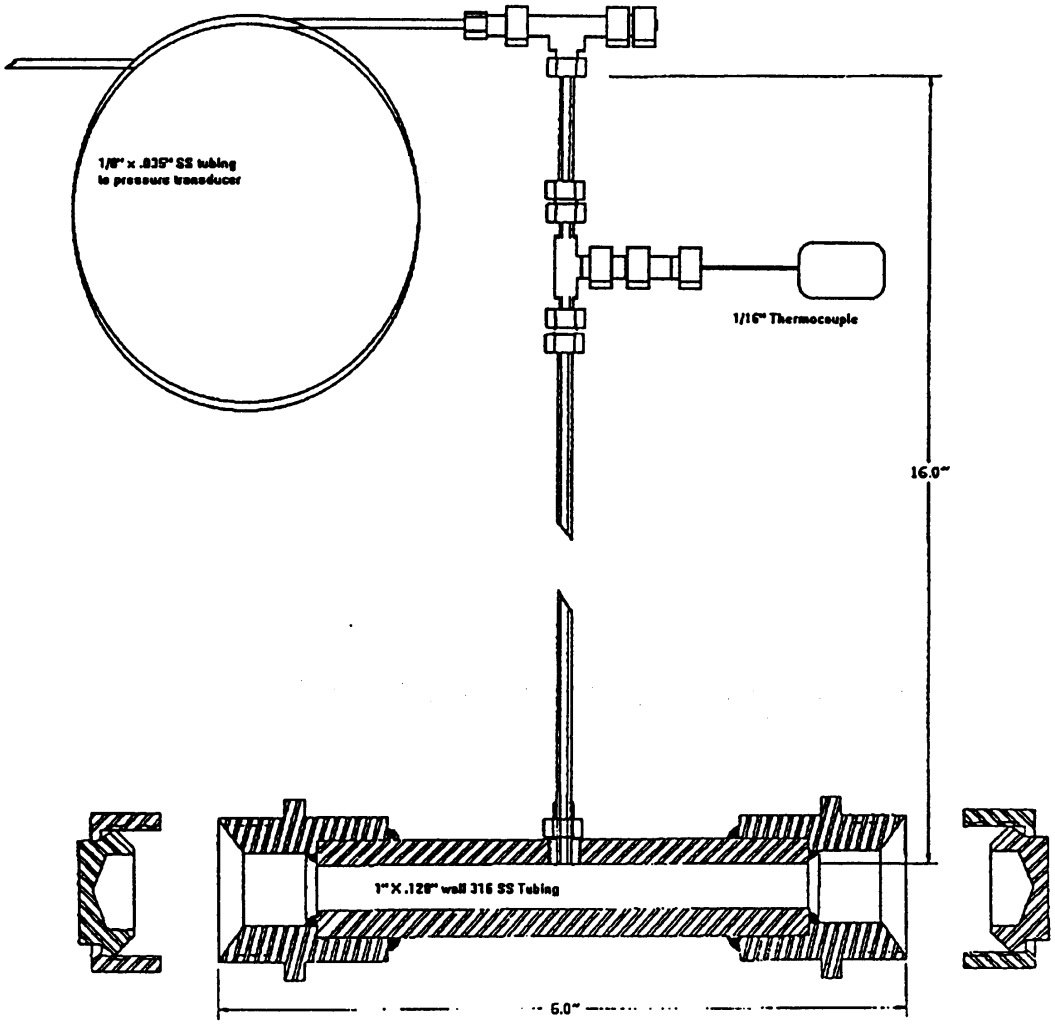



Figure 10. 50 mL Microautoclave Reactor for Catalytic Upgrading Studies.

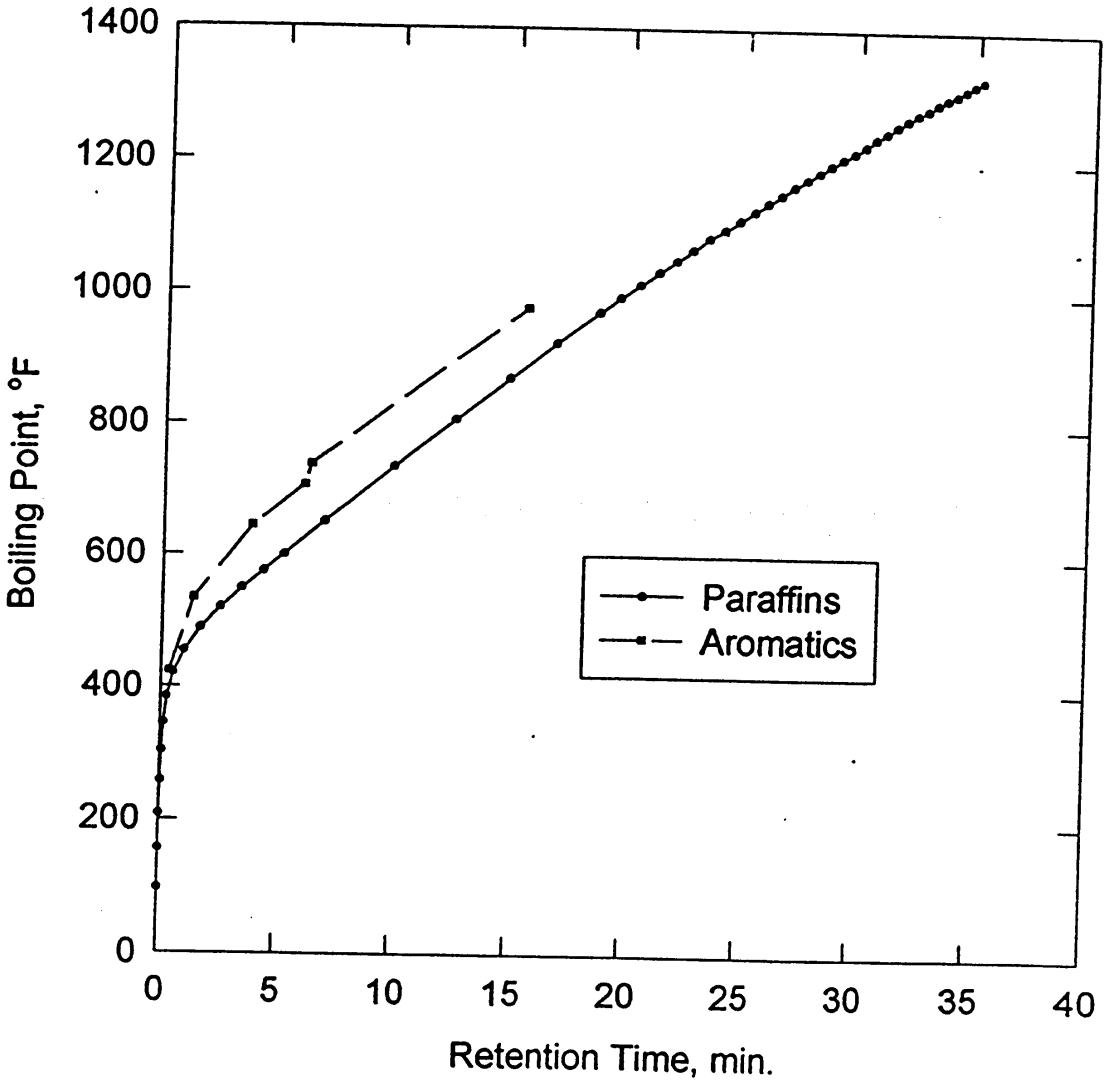



Figure 11. Retention Time Differences Between an n-alkane Mixture (to C120) and a Mixture of Condensed Aromatic Compounds.

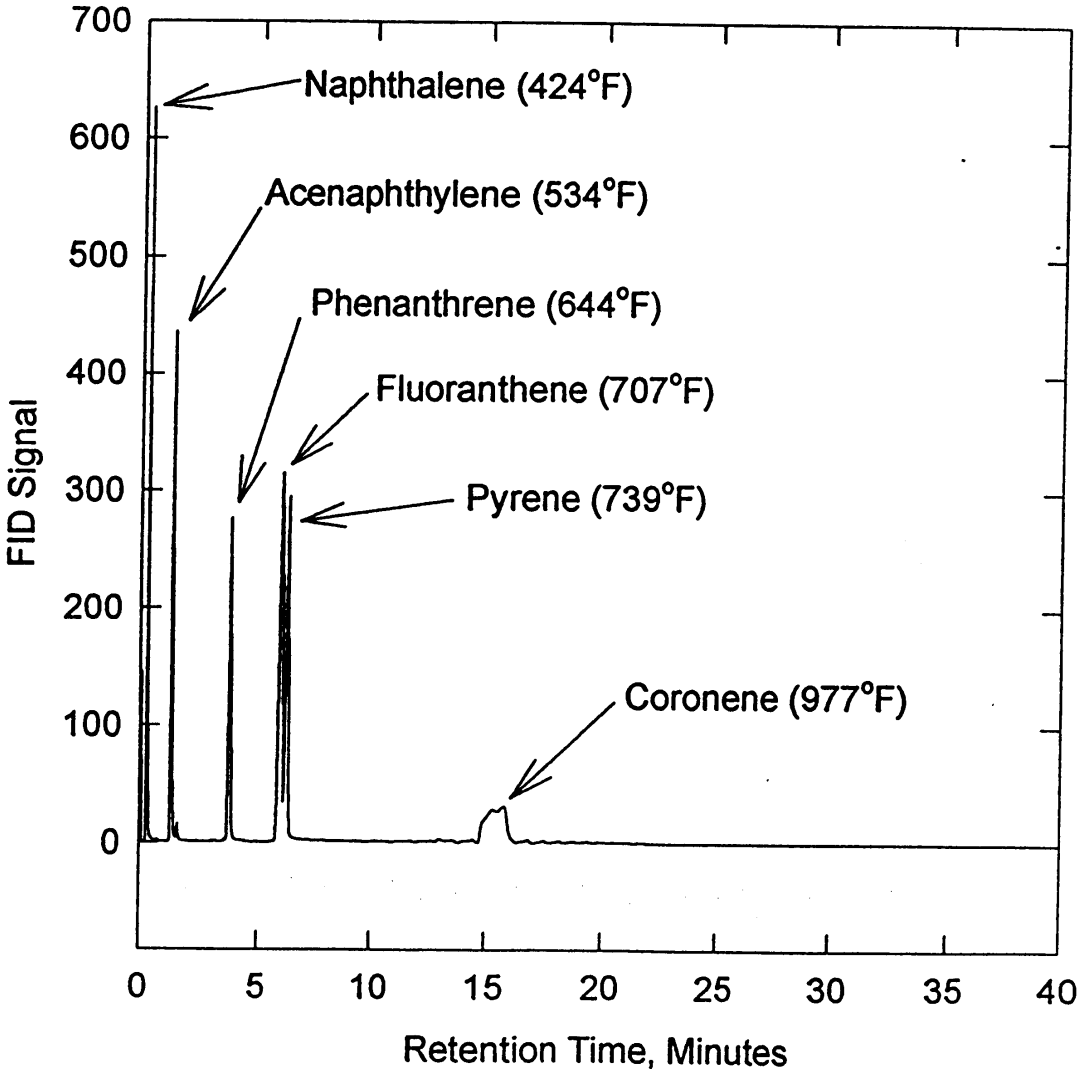



Figure 12. Gas Chromatograph of an Aromatic Mixture Under the High-Temperature Simulated Distillation Method.

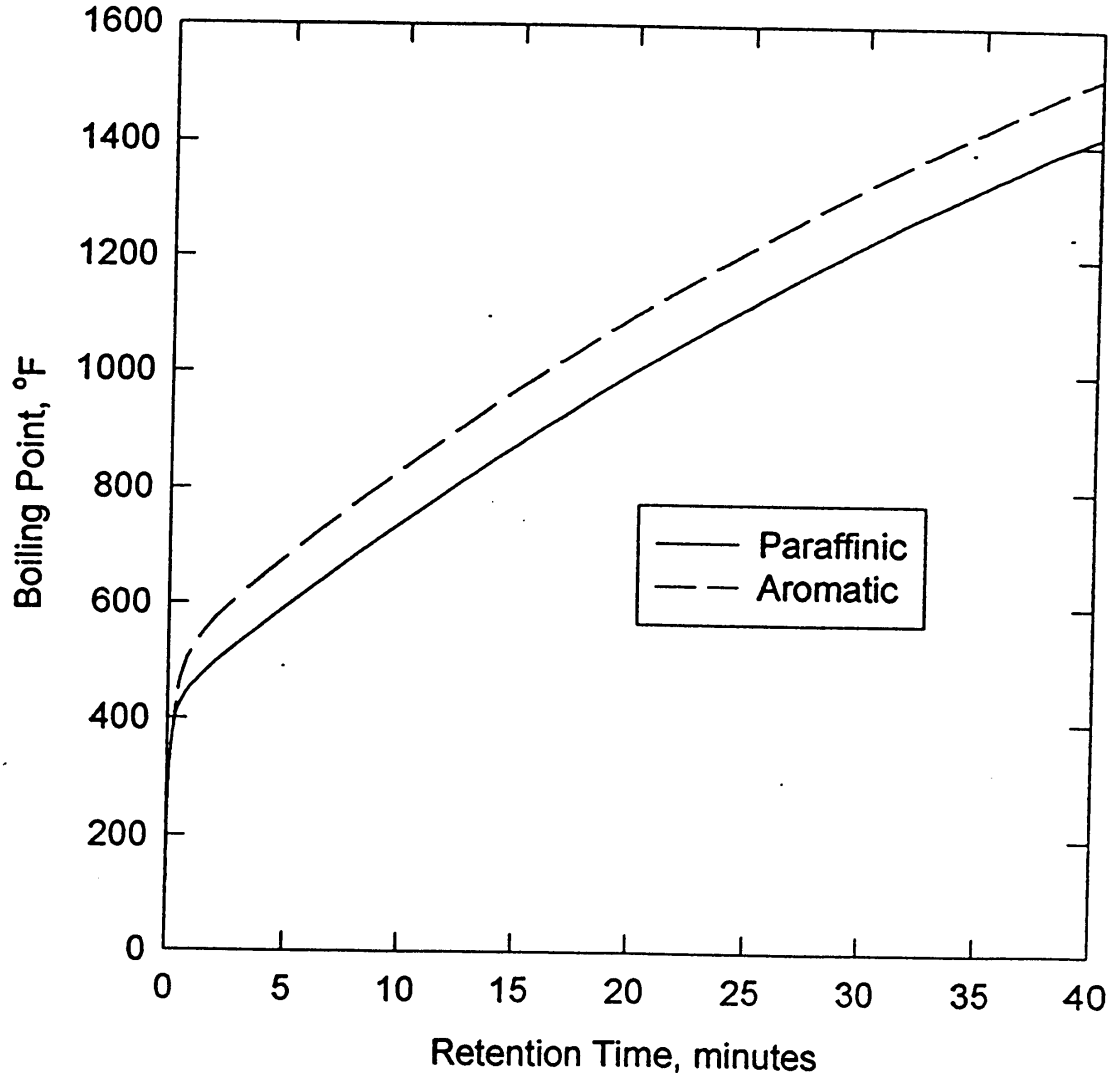



Figure 13. Paraffinic and Aromatic Calibration Curves Derived by Least-Squares Curve Fitting Analysis.

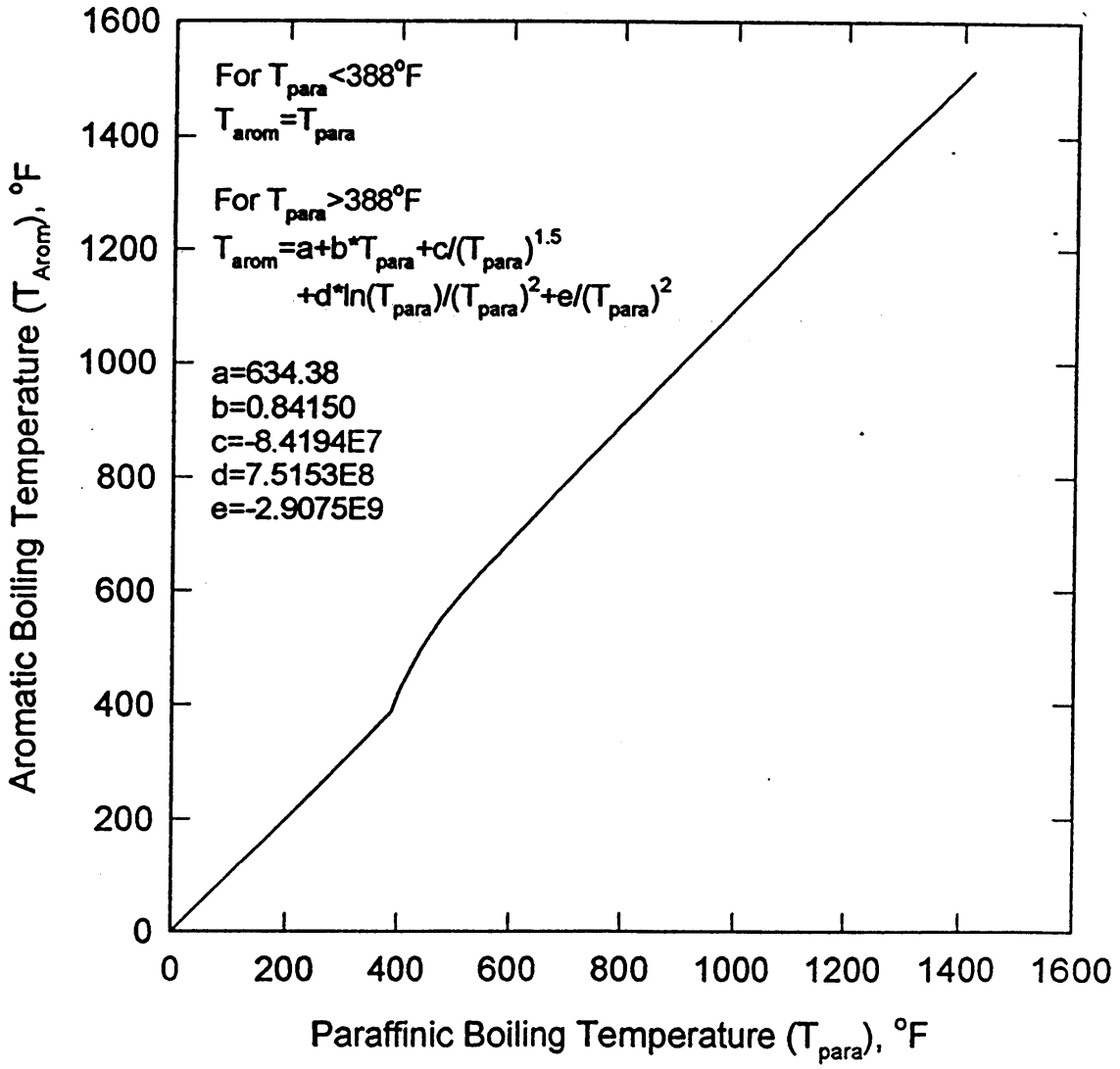



Figure 14. Aromatic Temperature Correction Derived from the Calibration Curves Presented in Figure 13.

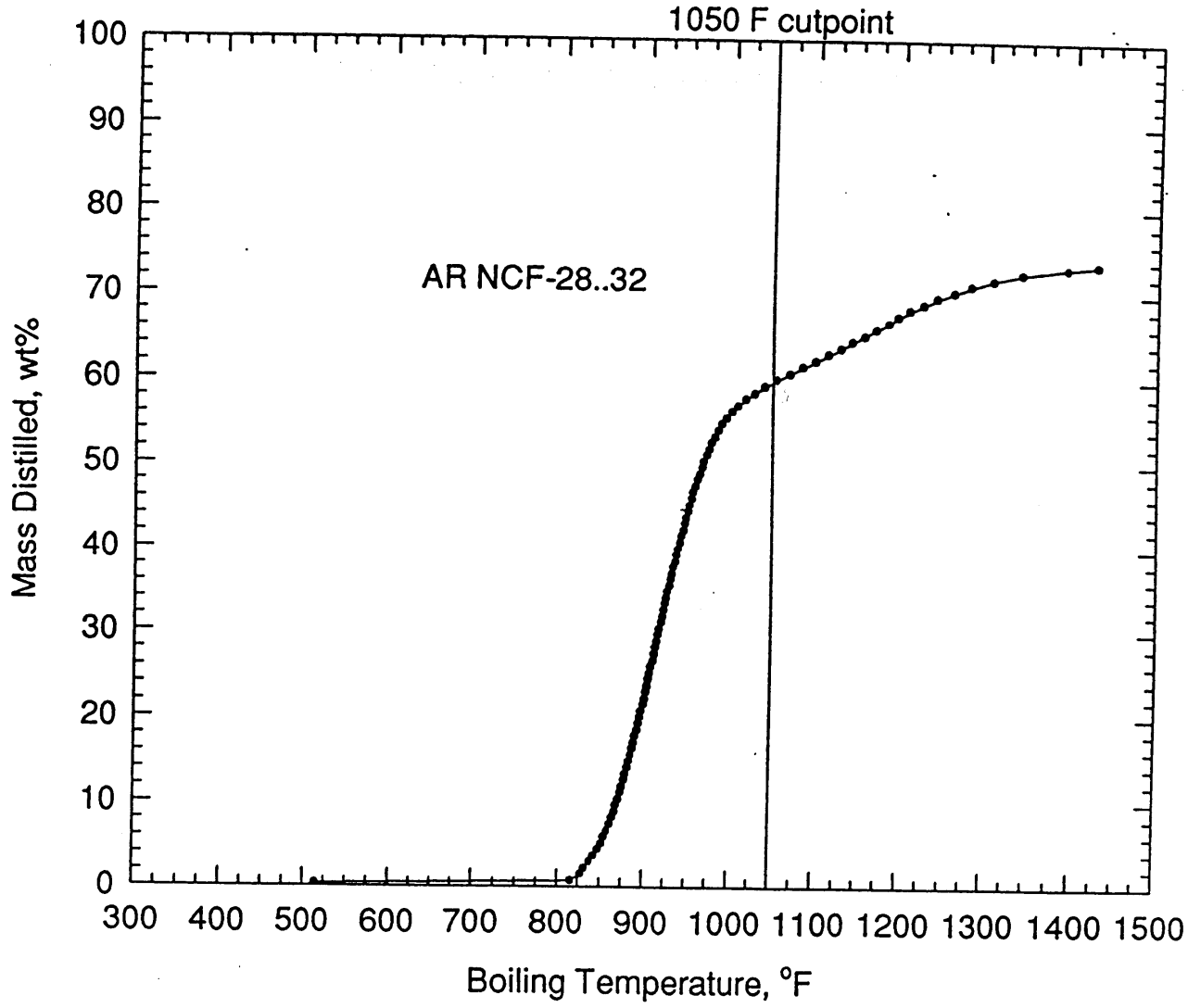



Figure 15. Simulated Distillation Results for Parametric Study Feedstock.
(High-Temperature Sim-Dist Analysis with Aromatic Correction)

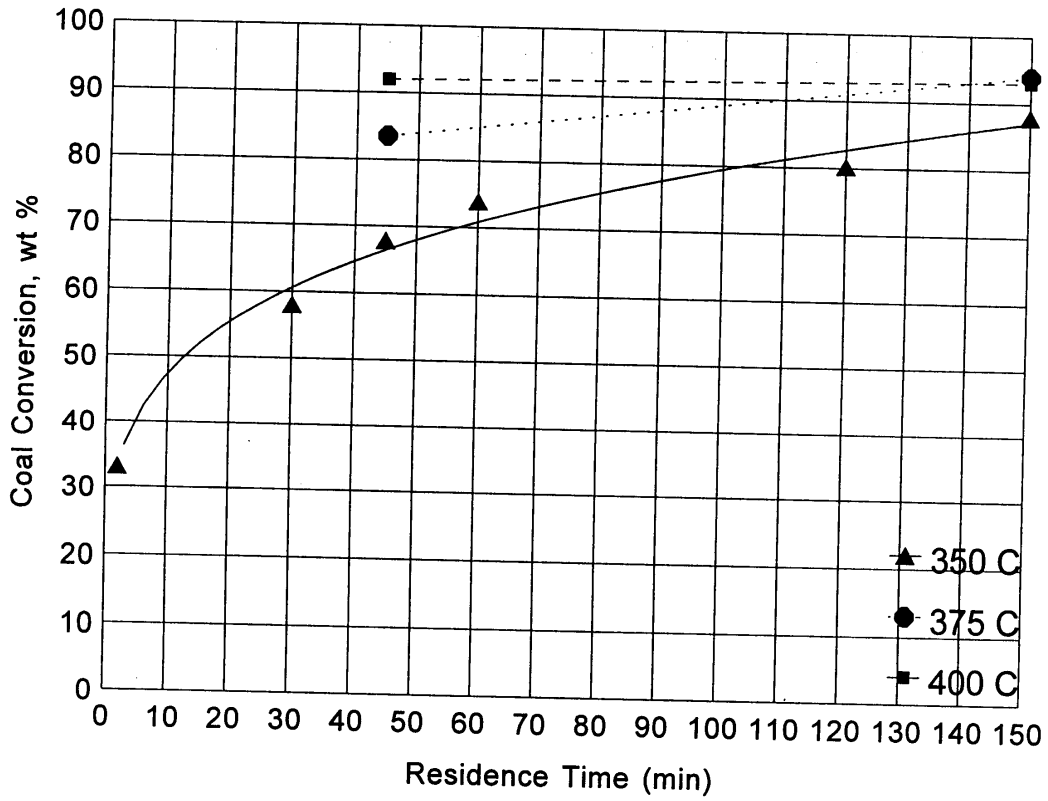



Figure 16. Coal Conversion as a Function of Temperature and Residence Time. Freedom Mine North Dakota Lignite; Solvent/Dry Coal = 2.2; HI"A"/Dry Coal = 1

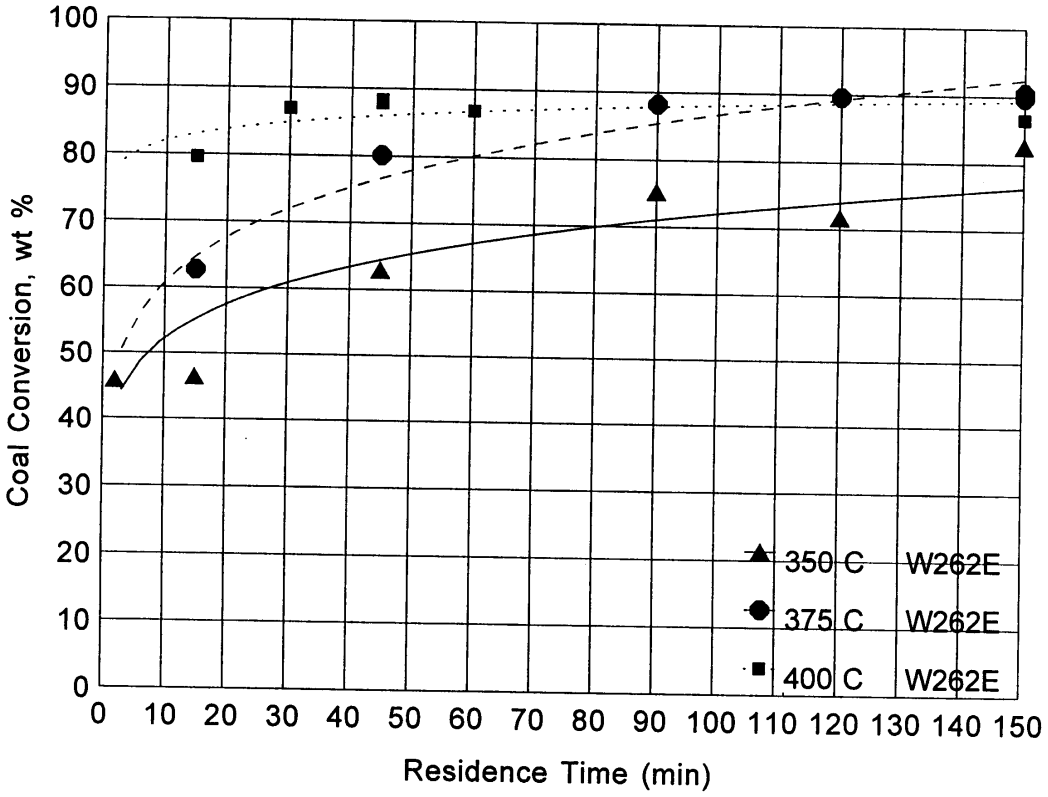



Figure 17. Coal Conversion as a Function of Temperature and Residence Time. Black Thunder Mine Subbituminous Coal; Solvent/Dry Coal = 2; Hydride Ion/Dry Coal = 1.

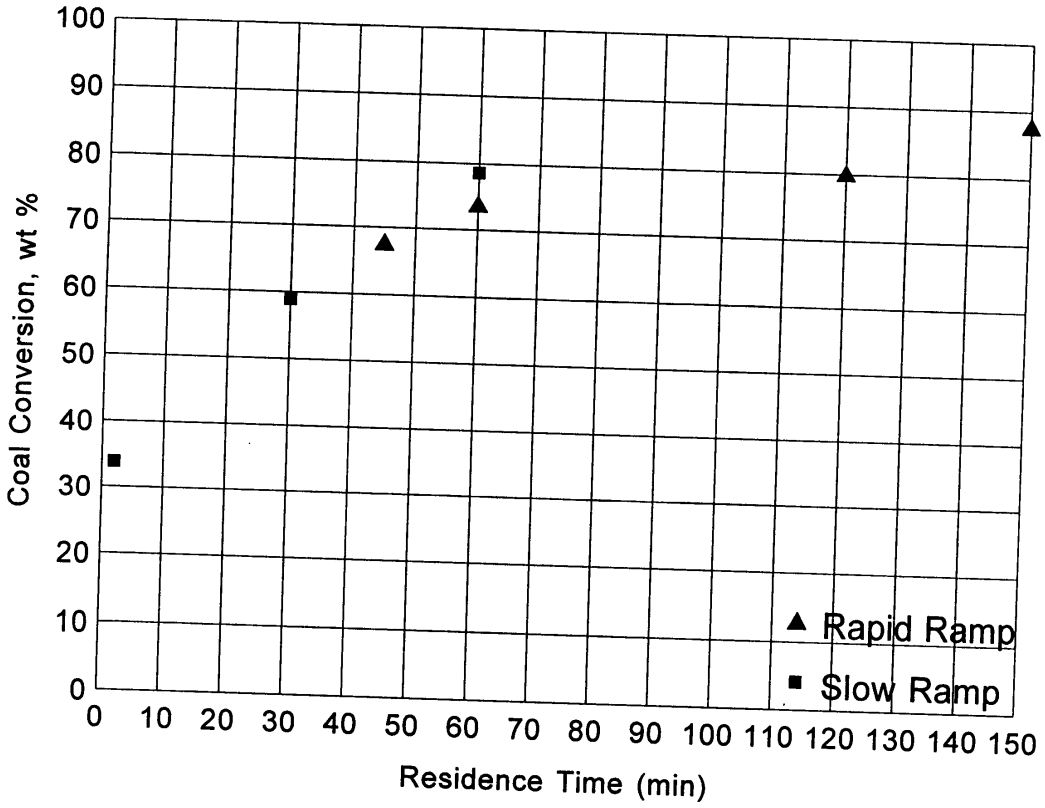



Figure 18. Coal Conversion as a Function of Heating Rate and Residence Time. North Dakota Lignite; V-1074/Dry Coal = 2.2; HI"A"/Dry Coal = 1.1

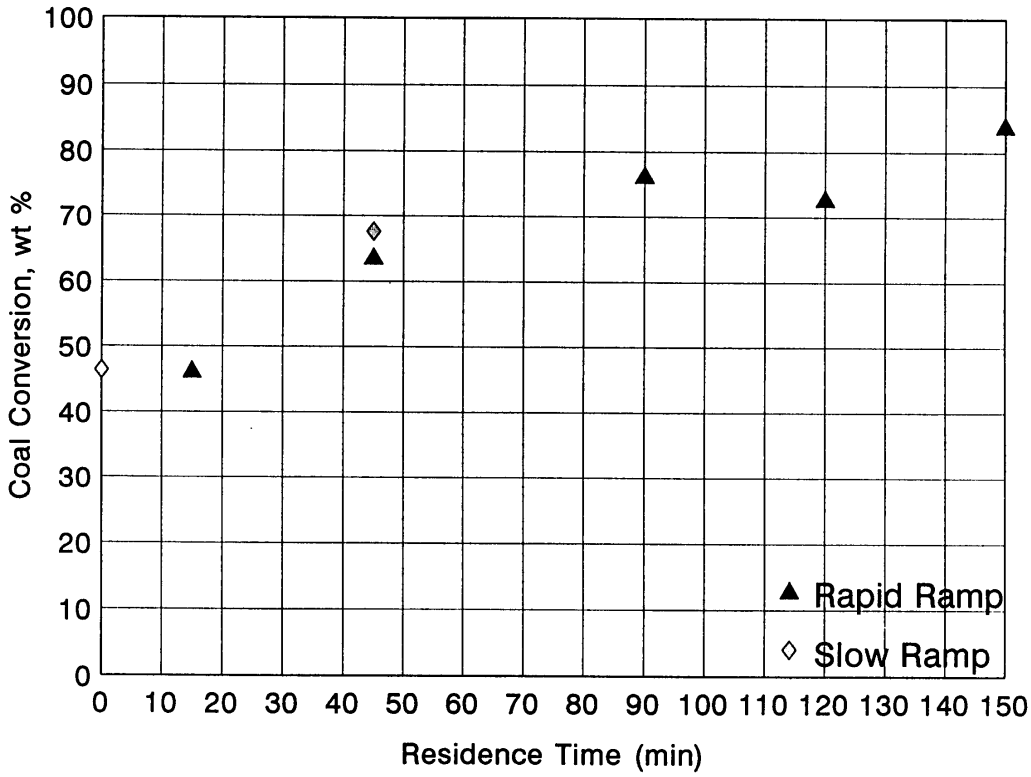



Figure 19. Coal Conversion as a Function of Heating Rate and Residence Time. Black Thunder Mine, V-1074/Dry Coal = 2; HI"A"/Dry Coal = 1

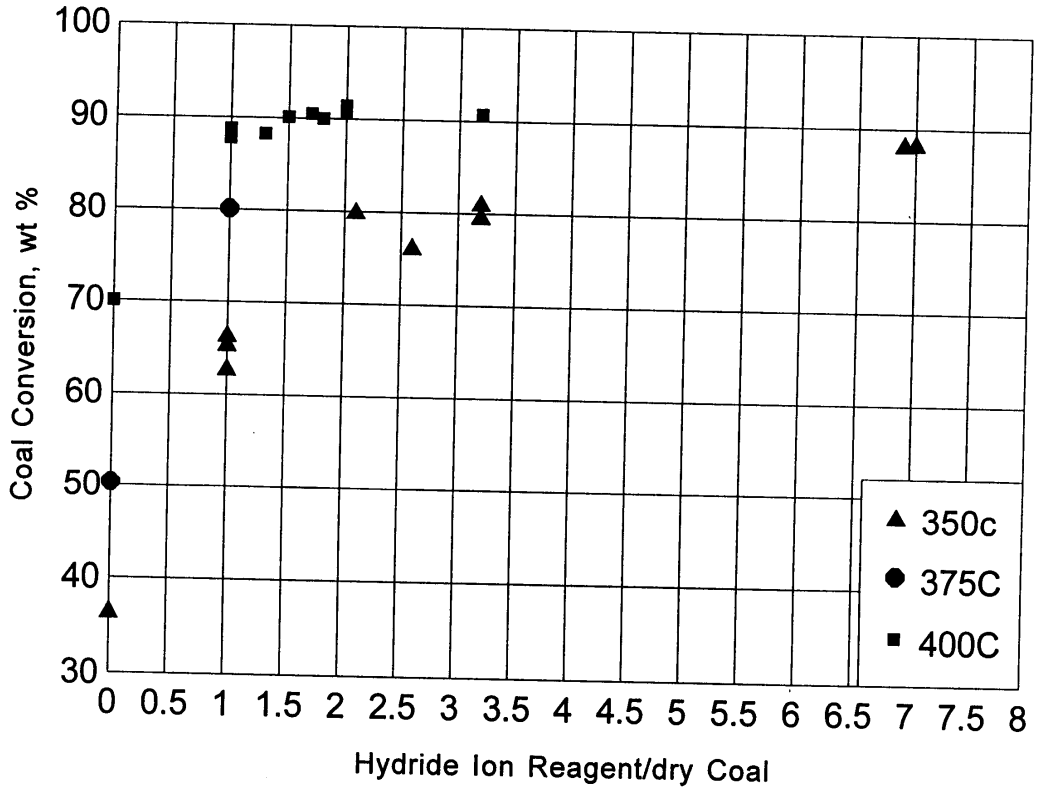



Figure 20. Coal Conversion vs HI"A"/Dry Coal Ratio.
Black Thunder Mine Subbituminous Coal, 45 min

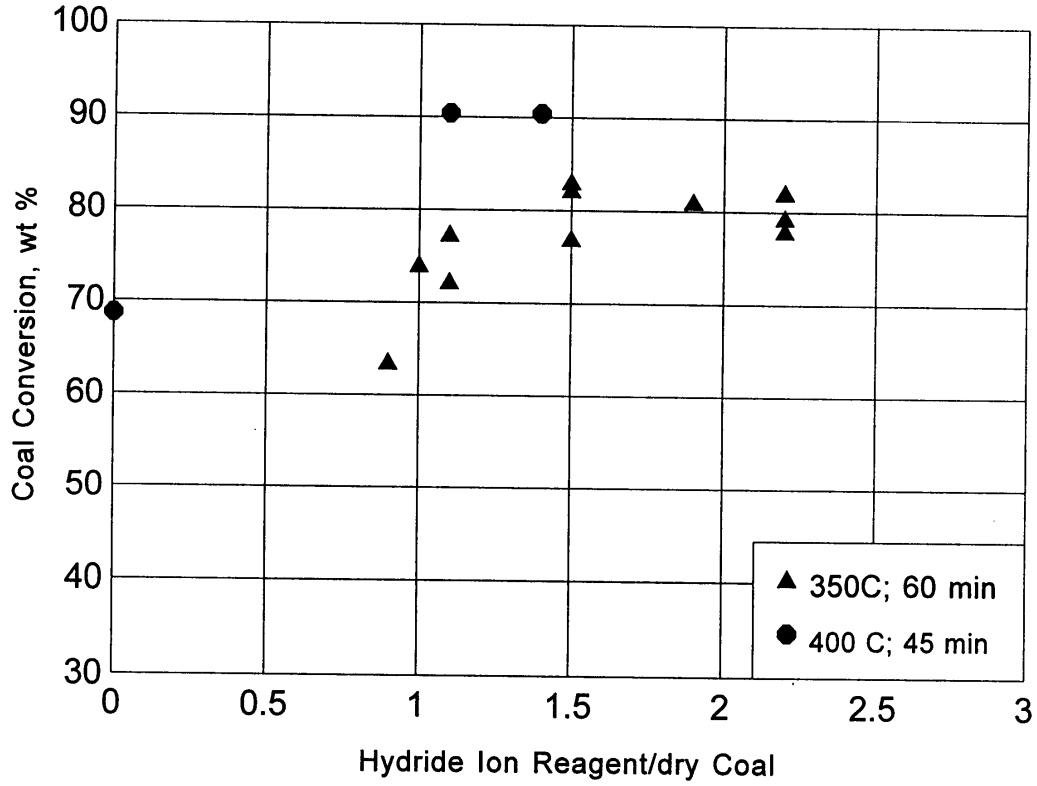



Figure 21. Coal Conversion vs HI"A"/Dry Coal Ratio.
Low-Ash Freedom Mine Lignite

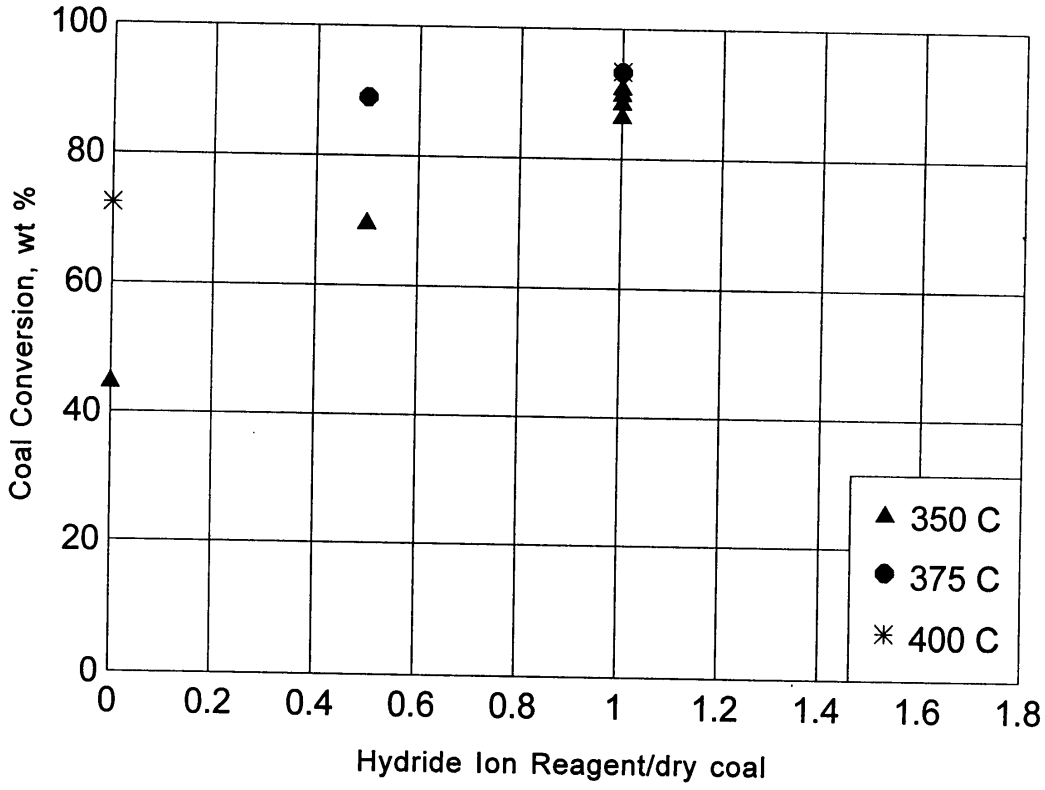



Figure 22. Coal Conversion vs HI "A"/Dry Coal Ratio
Ohio 11 Mine Bituminous Coal, 60 min, HI "A"/Dry Coal = 1

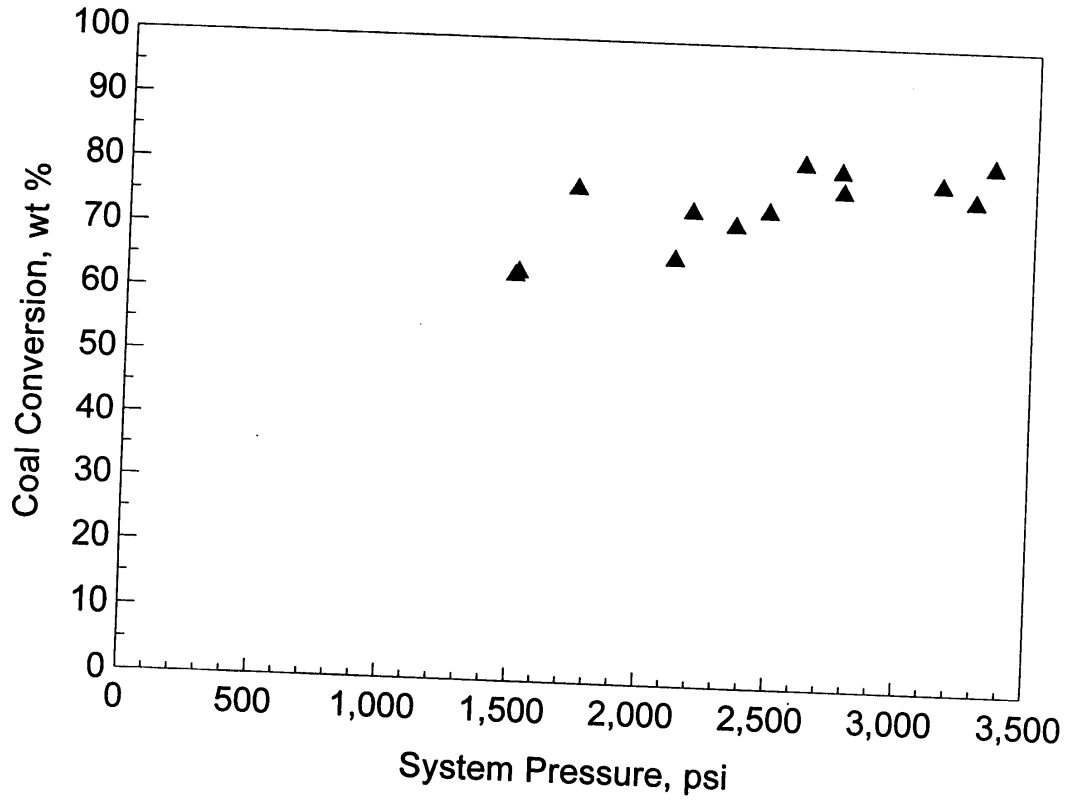



Figure 23. Coal Conversion vs System Pressure.
Freedom Mine, North Dakota Lignite, 350 °C, 60 min

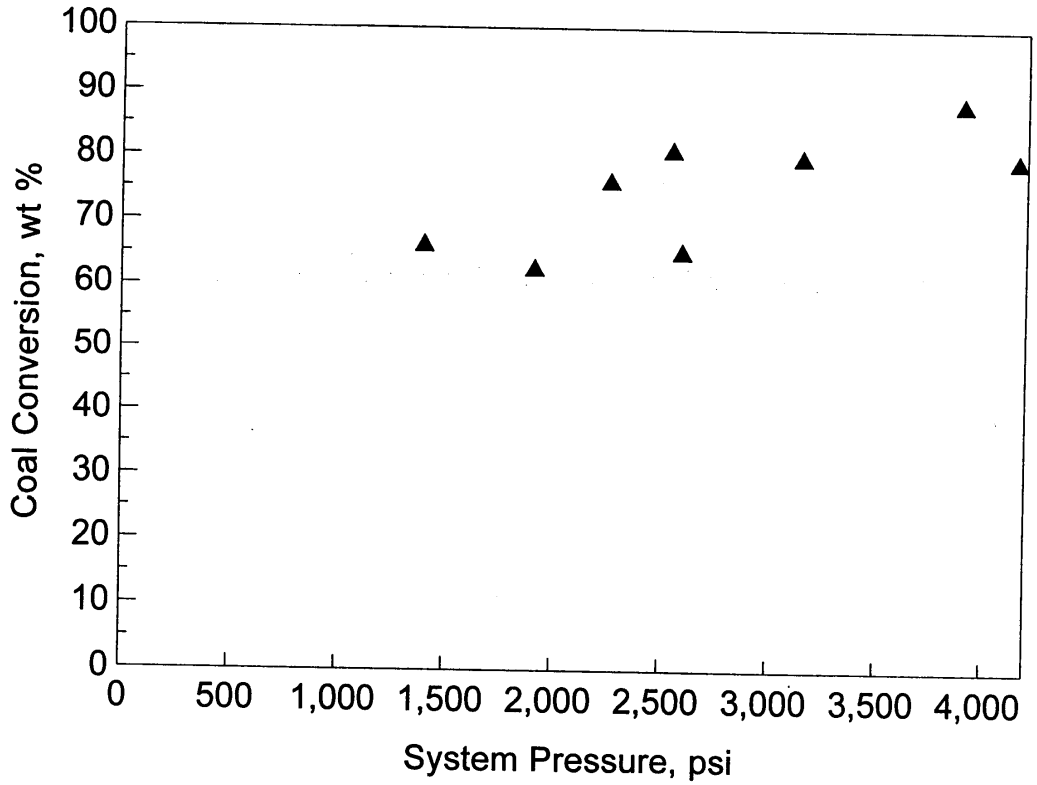



Figure 24. Coal Conversion vs System Pressure.
Black Thunder Mine, Subbituminous Coal, 350 °C, 45 min

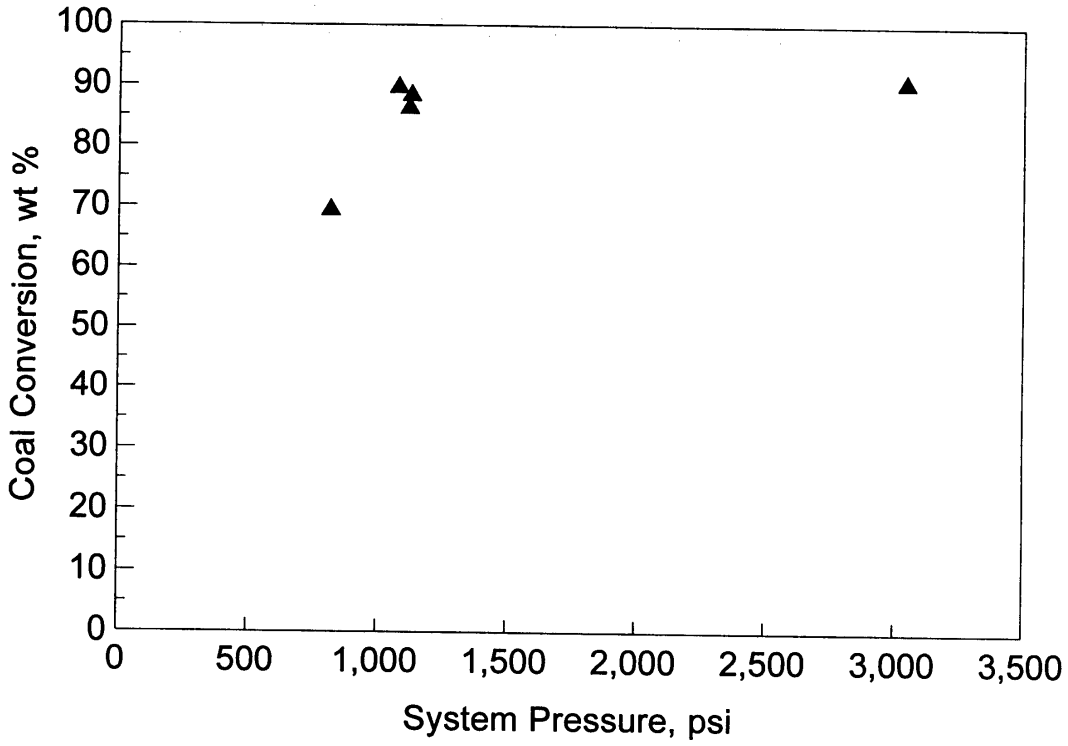



Figure 25. Coal Conversion vs. System Pressure.
Ohio 11 Mine Bituminous Coal, 350 °C, 60 min

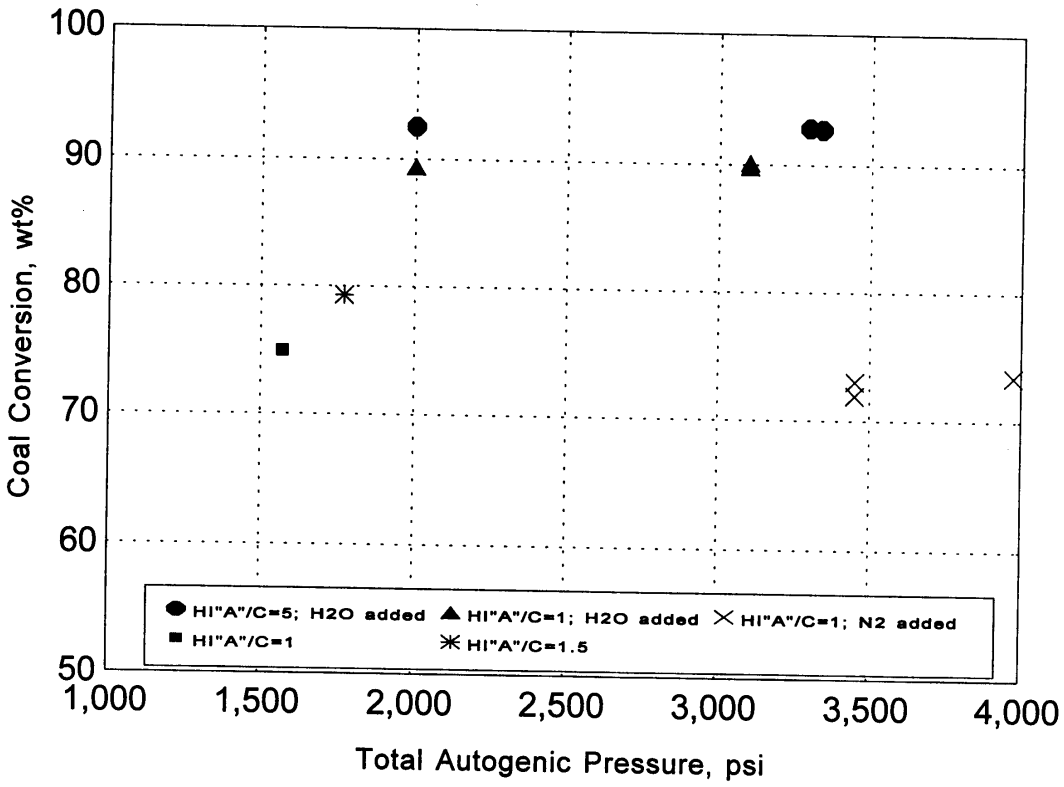
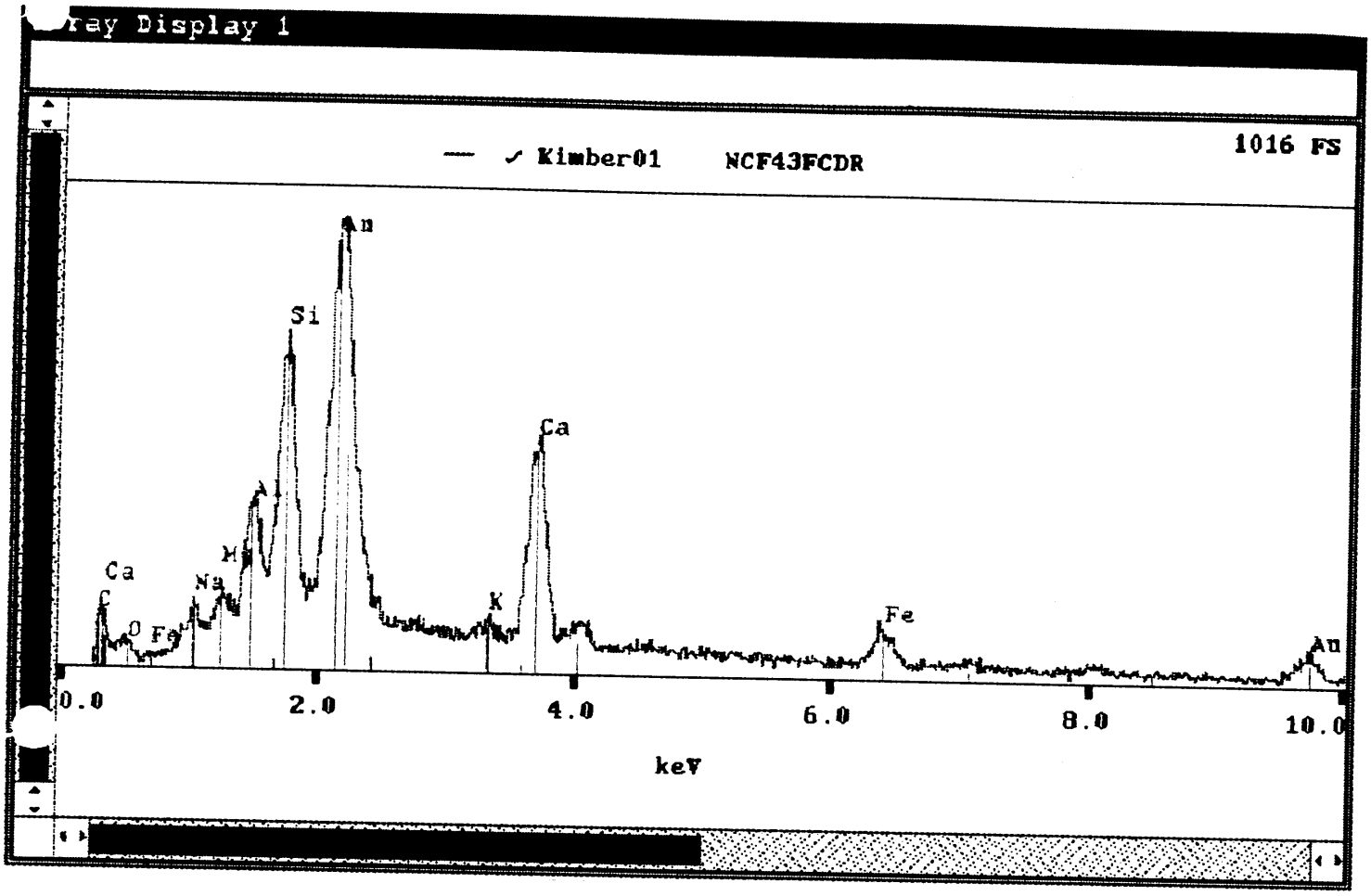



Figure 26. Coal Conversion vs. System Pressure.
Glenharold Mine Lignite; 350 °C; 60 min



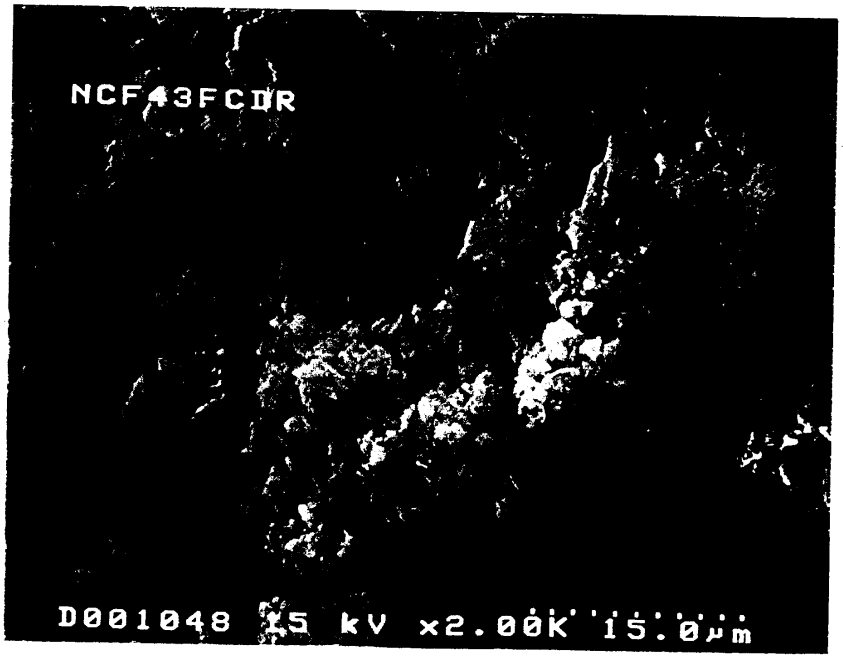




Figure 27. SEM of a Dried Filter Cake Derived From Glenharold Lignite.

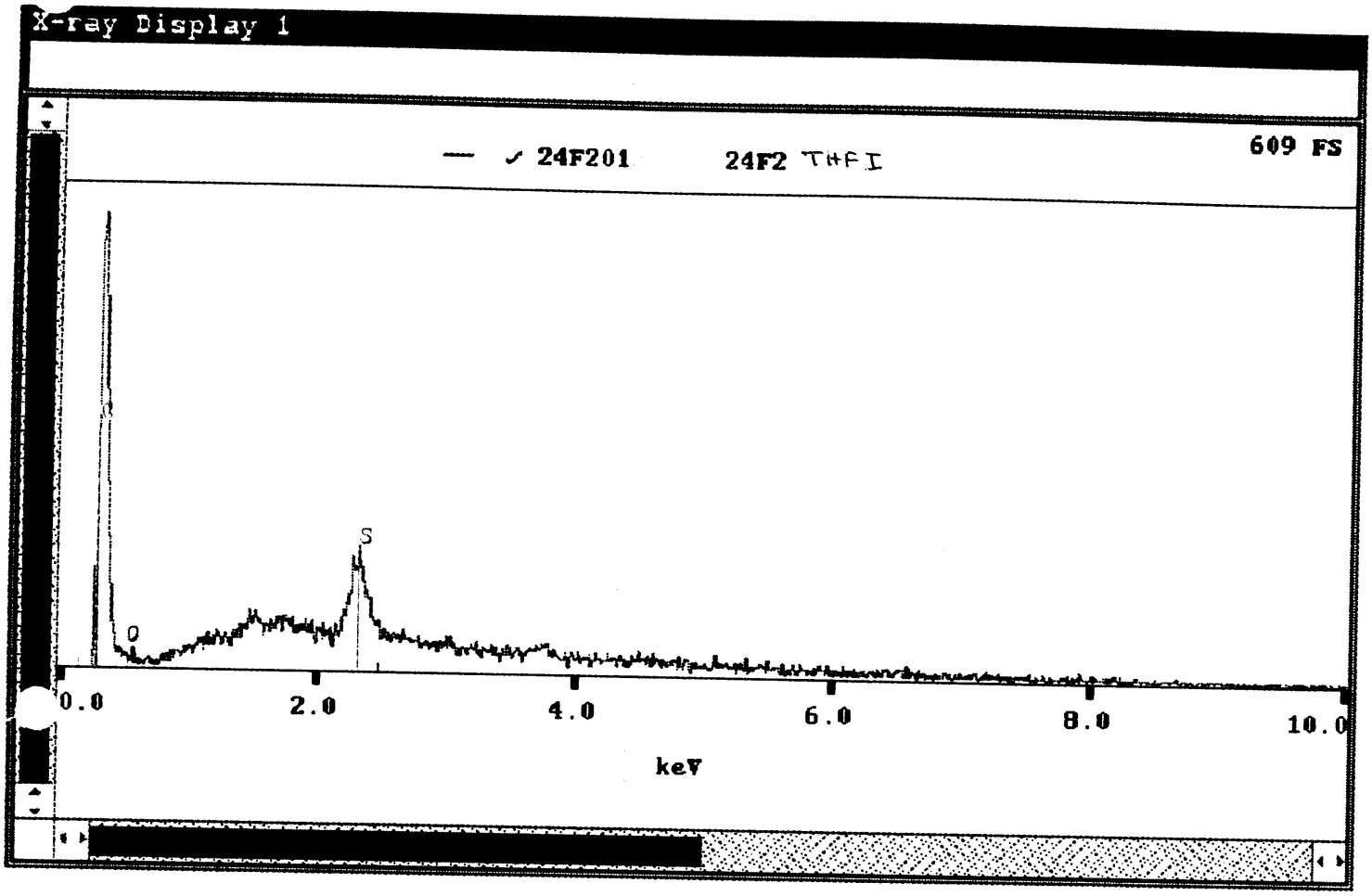
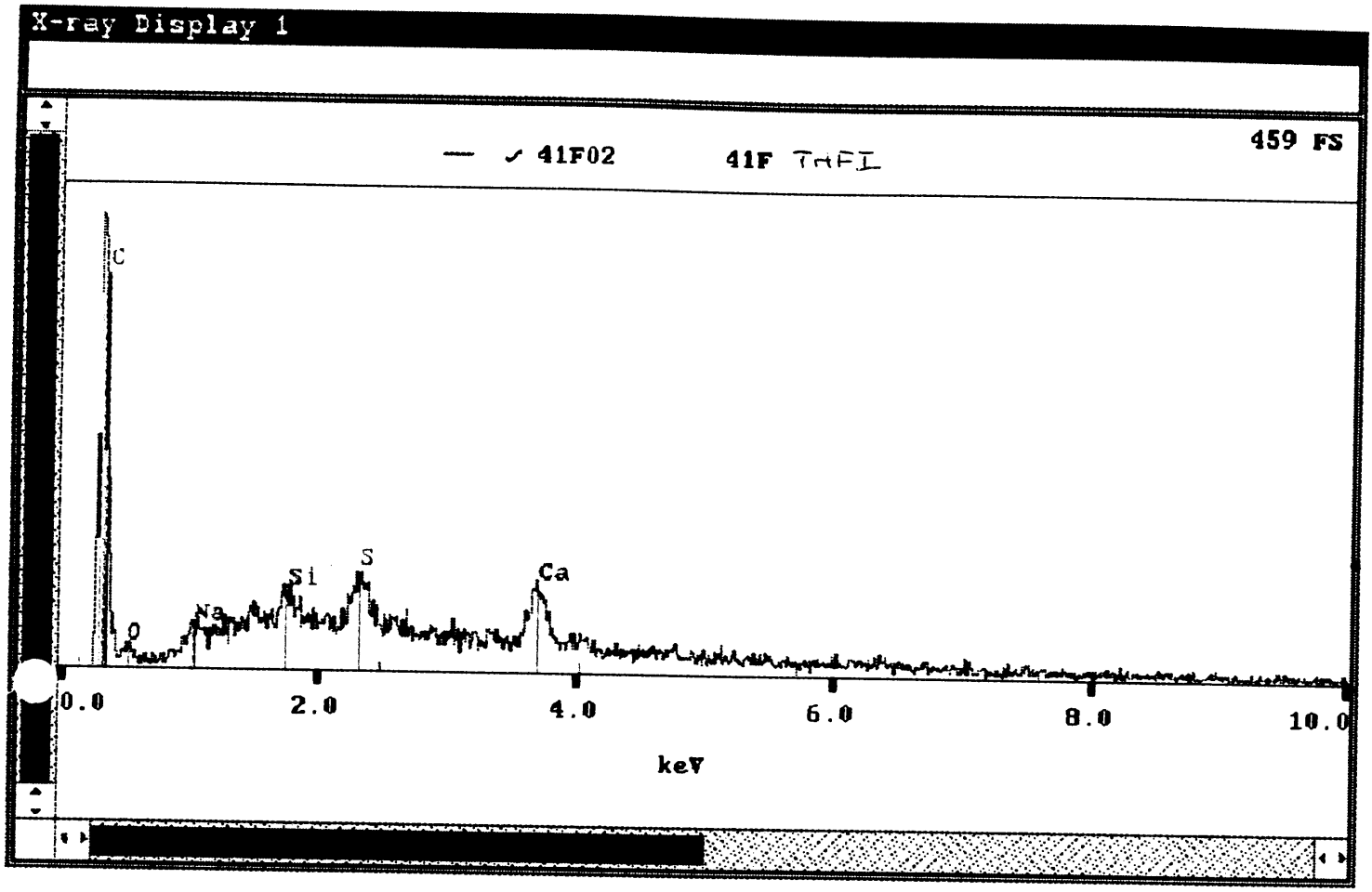




Figure 28. SEM of Filtrate THF Insolubles - Ohio 11 Coal.



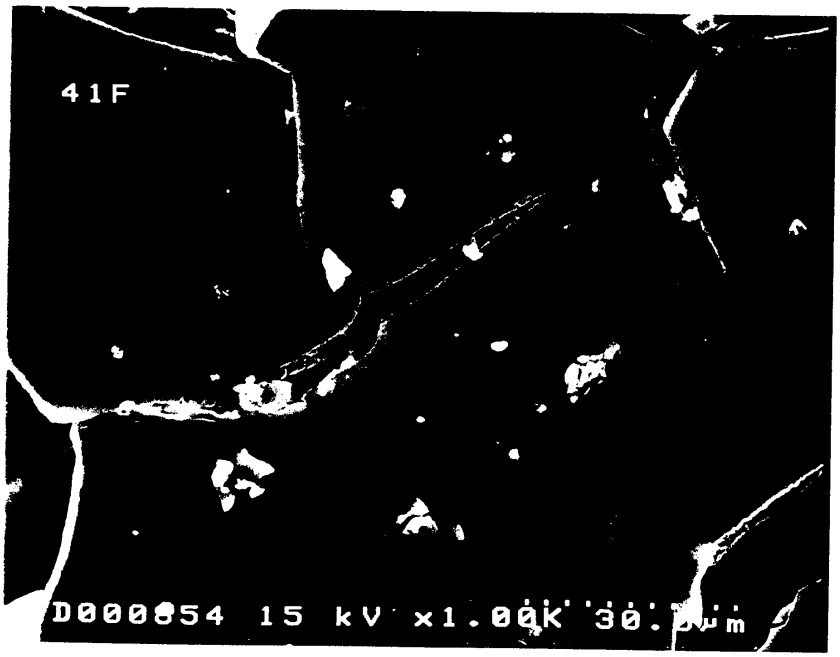




Figure 29. SEM of Filtrate THF Insolubles - Glenharold Lignite.

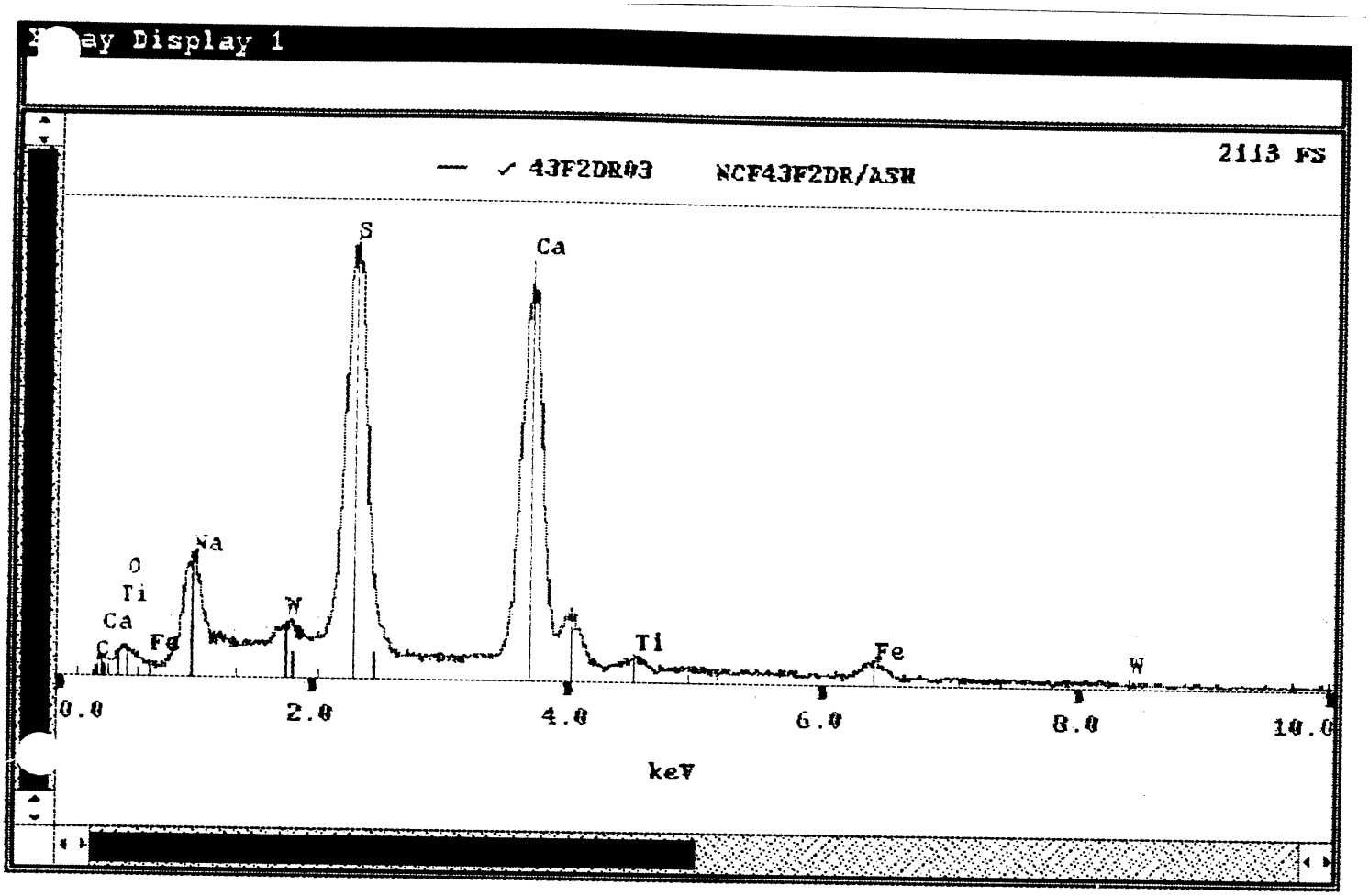




Figure 30. SEM of Ashed Filtrate - Glenharold Lignite.

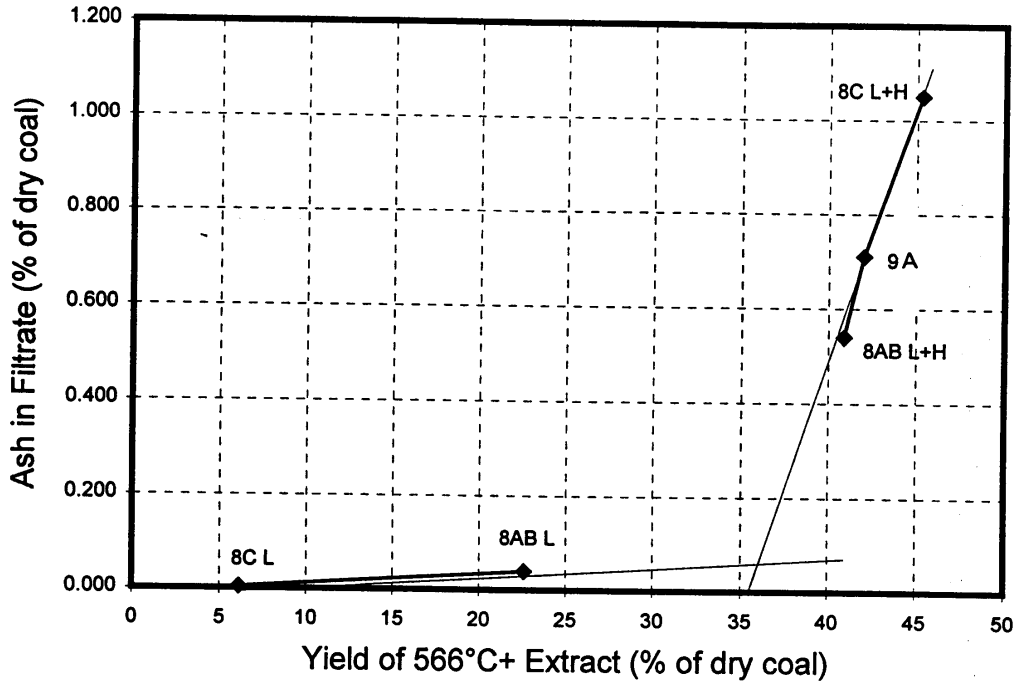



Figure 31. Ash in Filtrate vs. Cumulative Yield of 566 °C$^{+}$.

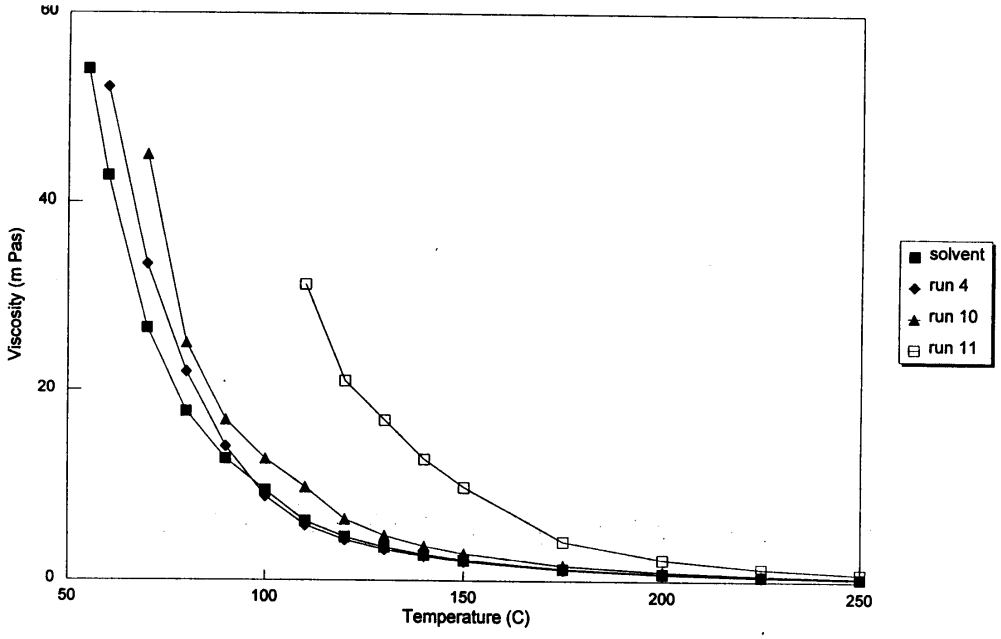



Figure 32. Viscosity of Coal Solutions.

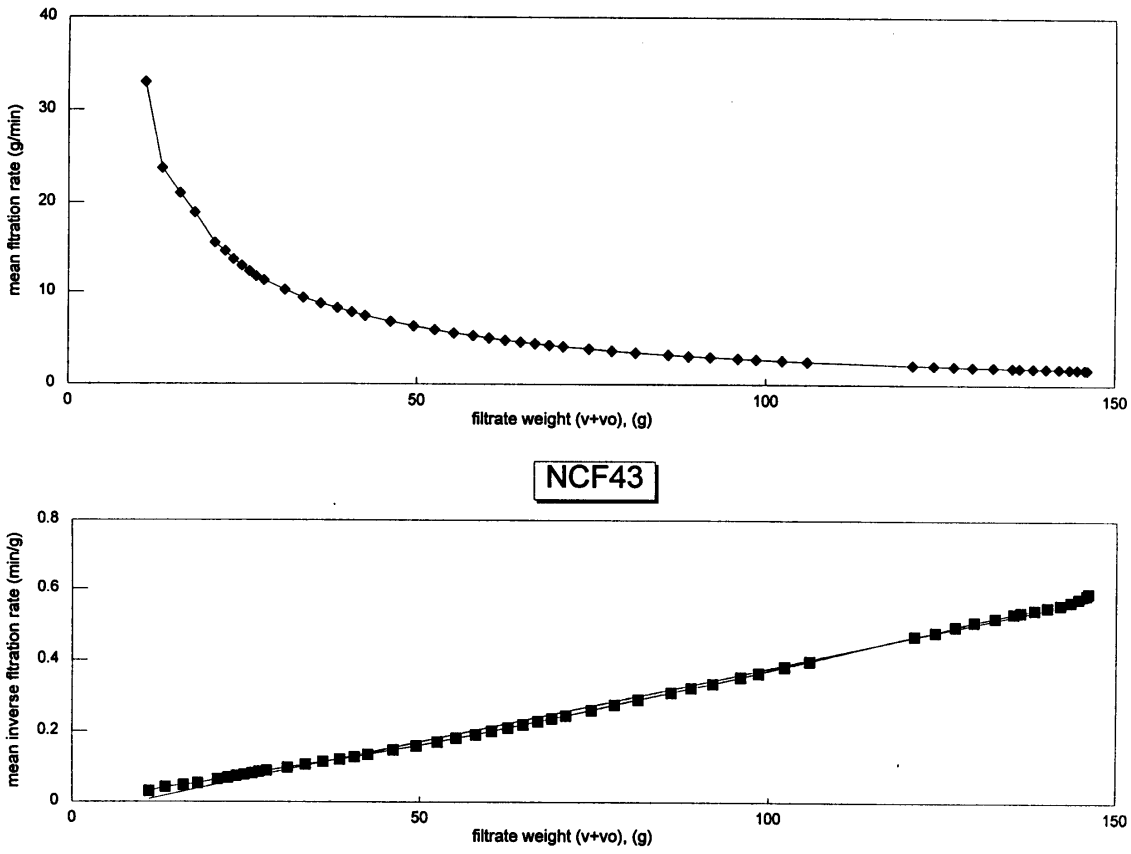



Figure 33. Filtration of 9a-LA.

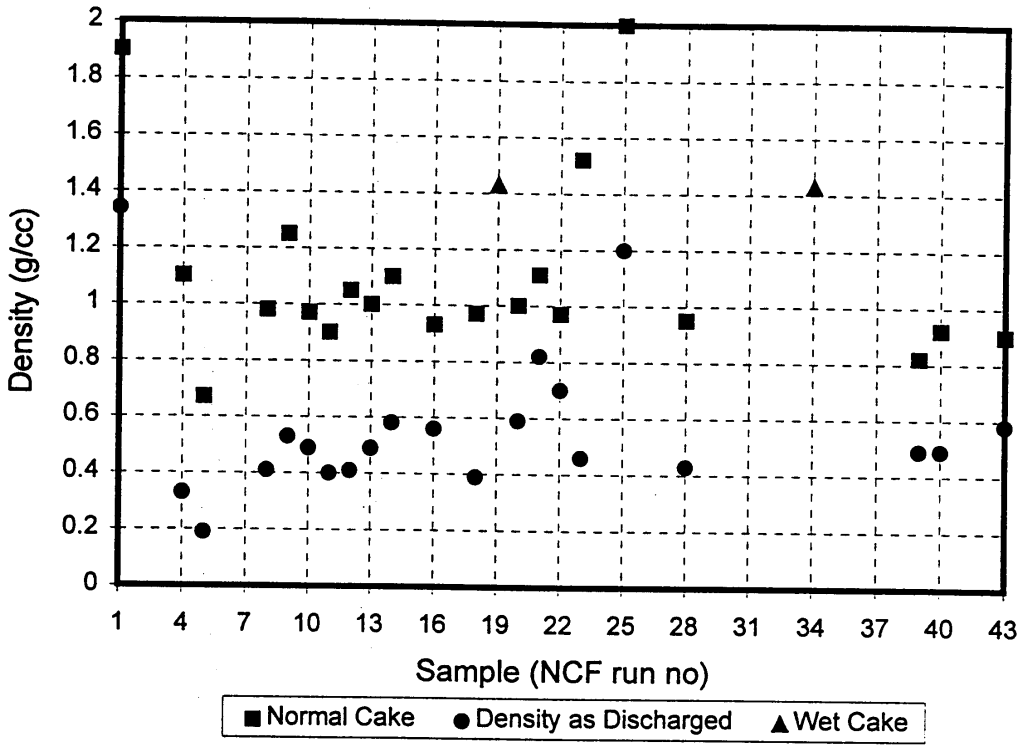



Figure 34. Filter Cake Density.

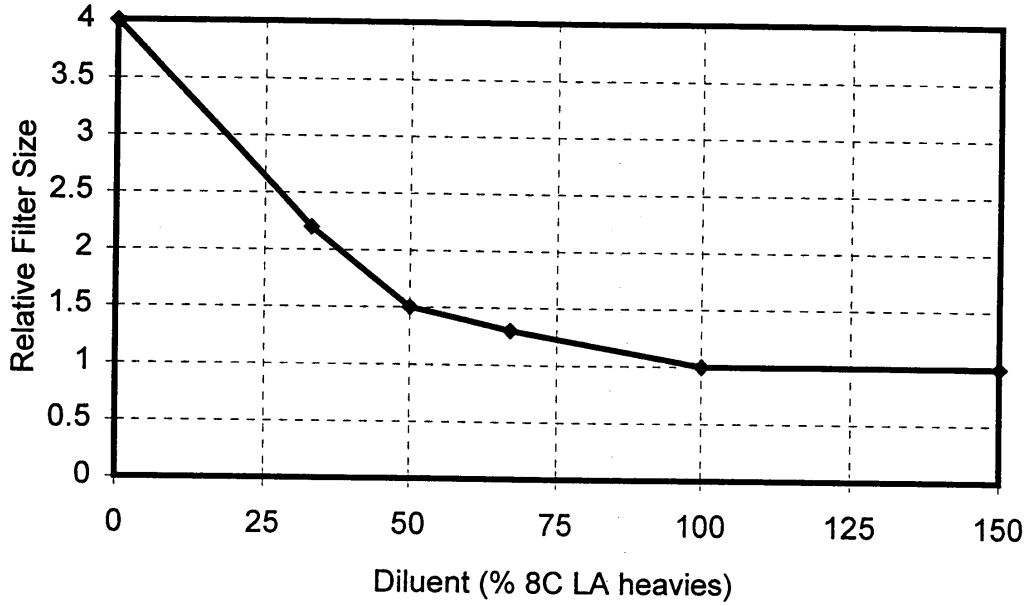



Figure 35. Effect of Diluent on Filter Area Required for a Fixed Throughput of Extract and Solids.

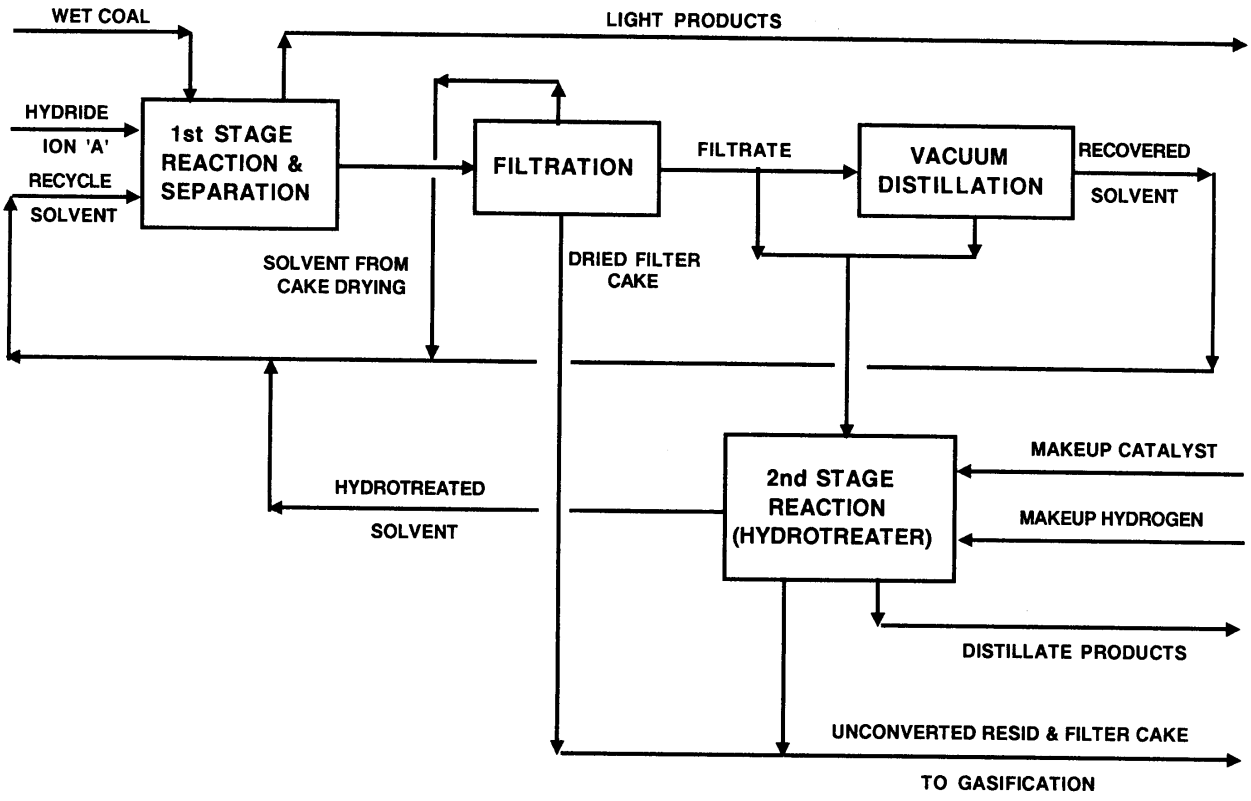
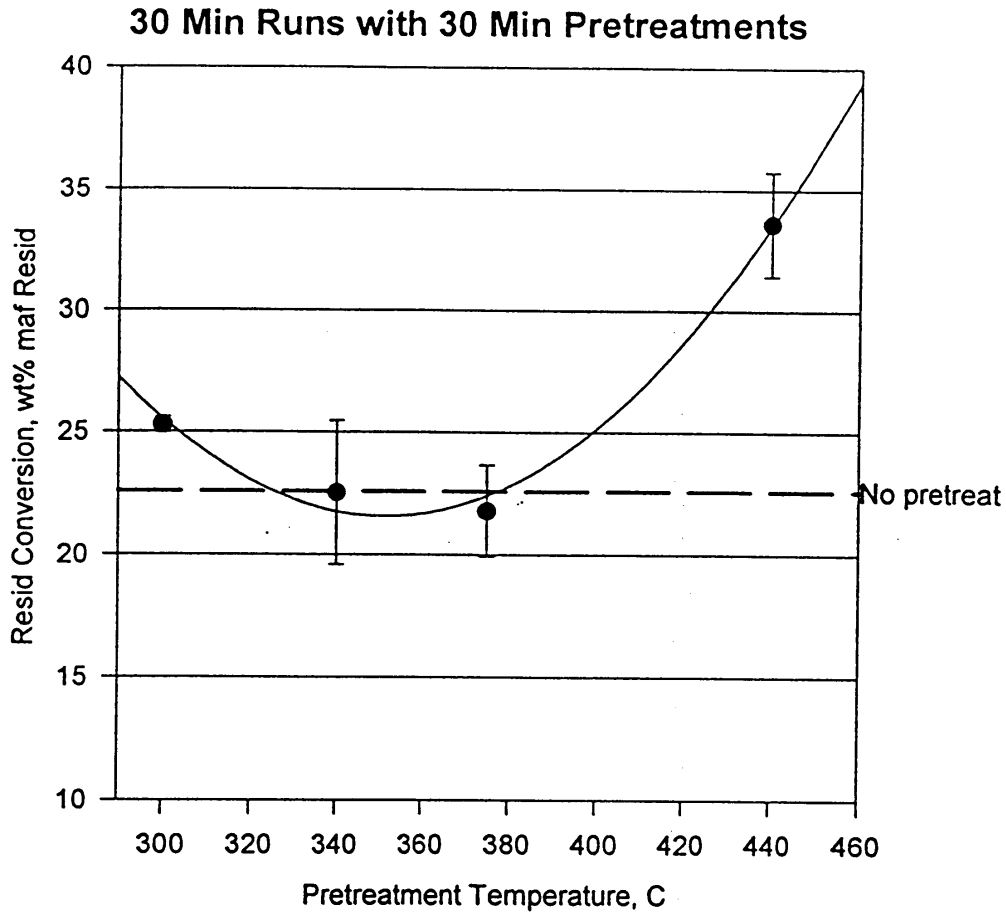
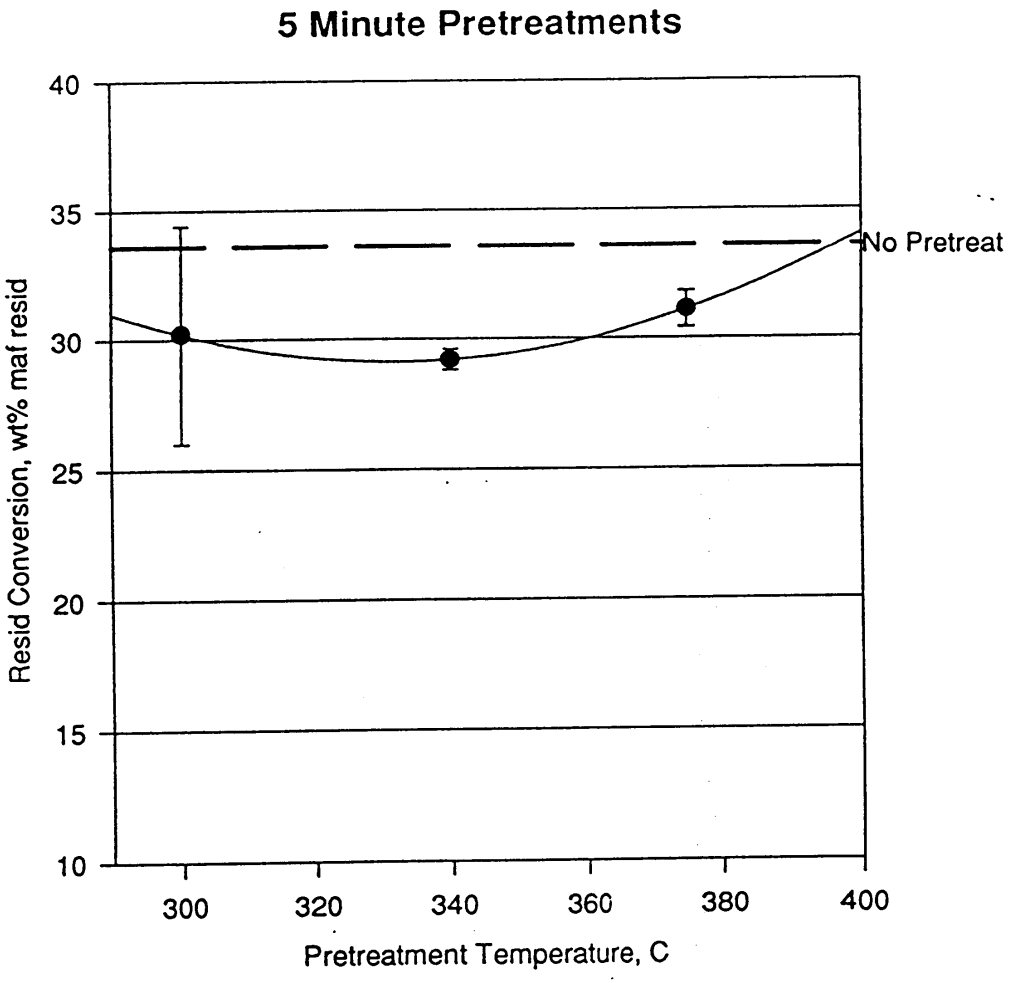



Figure 36. CONSOL NCLC - Simplified Block Flow Diagram
Integrated Liquefaction System.



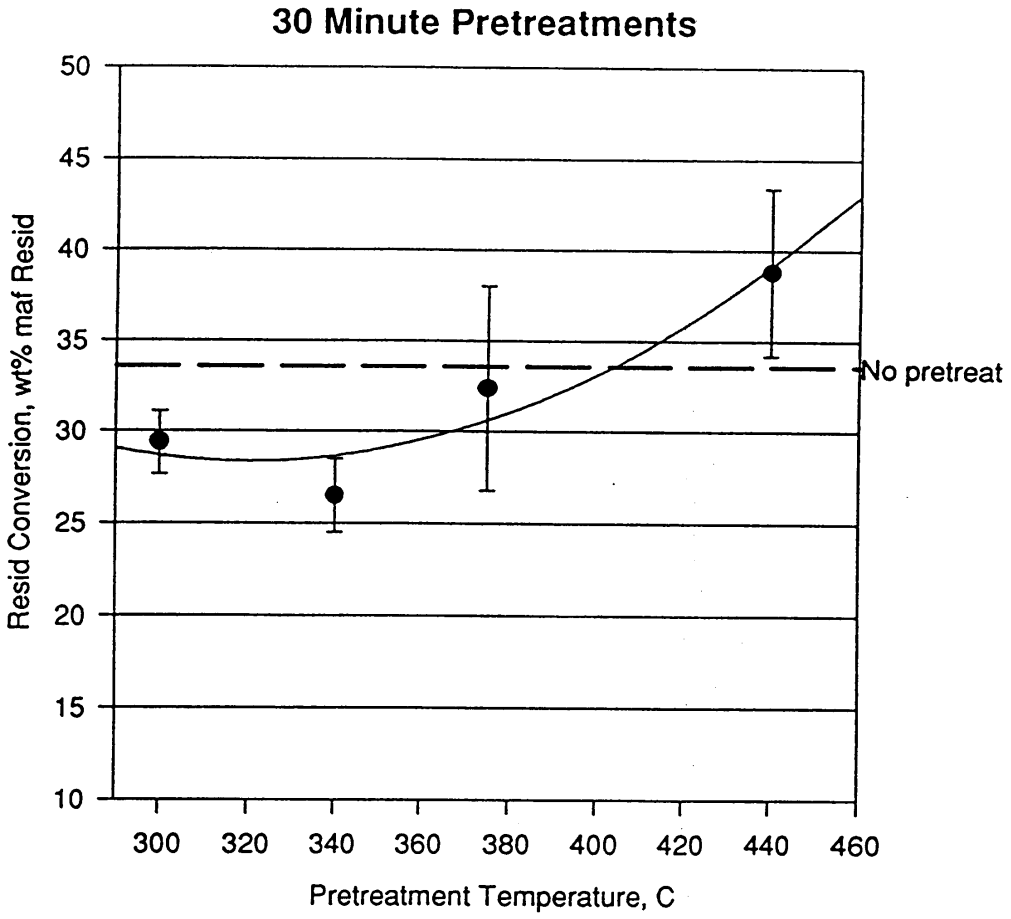

Hydrotreatment at 440 C for 30 minutes
1000 ppmw Mo (Molyvan L, feed basis) in R-258A deashed resid
10.1 MPa total pressure (cold), 2% $H_2S$ in $H_2$
566 C+ resid conversion, SIMDIS checked

Figure 37. Effect of 30 min Pretreatment on Resid Conversion in 30 min Reactions. (Resid conversion is shown for 566 °C$^+$ material. Cold charge pressure was 10.1 MPa hydrogen mixture containing 2% $H_2S$.




Hydrotreatment at 440 C for 60 minutes
1000 ppmw Mo (Molyvan L, feed basis) in R-258A deashed resid

Figure 38. Effect of 5 min Pretreatment on Resid Conversion in 60 min Reactions. (Resid conversion is shown for 566 °C$^+$ material. Cold charge pressure was 10.1 MPa hydrogen mixture containing 2% $H_2S$.




Hydrotreatment at 440 C for 60 minutes
1000 ppmw Mo (Molyvan L, feed basis) in R-258A deashed resid

Figure 39 Effect of 30 min Pretreatment on Resid Conversion in 60 min Reactions. (Resid conversion is shown for 566 °C$^+$ material. Cold charge pressure was 10.1 MPa hydrogen mixture containing 2% $H_2S$.

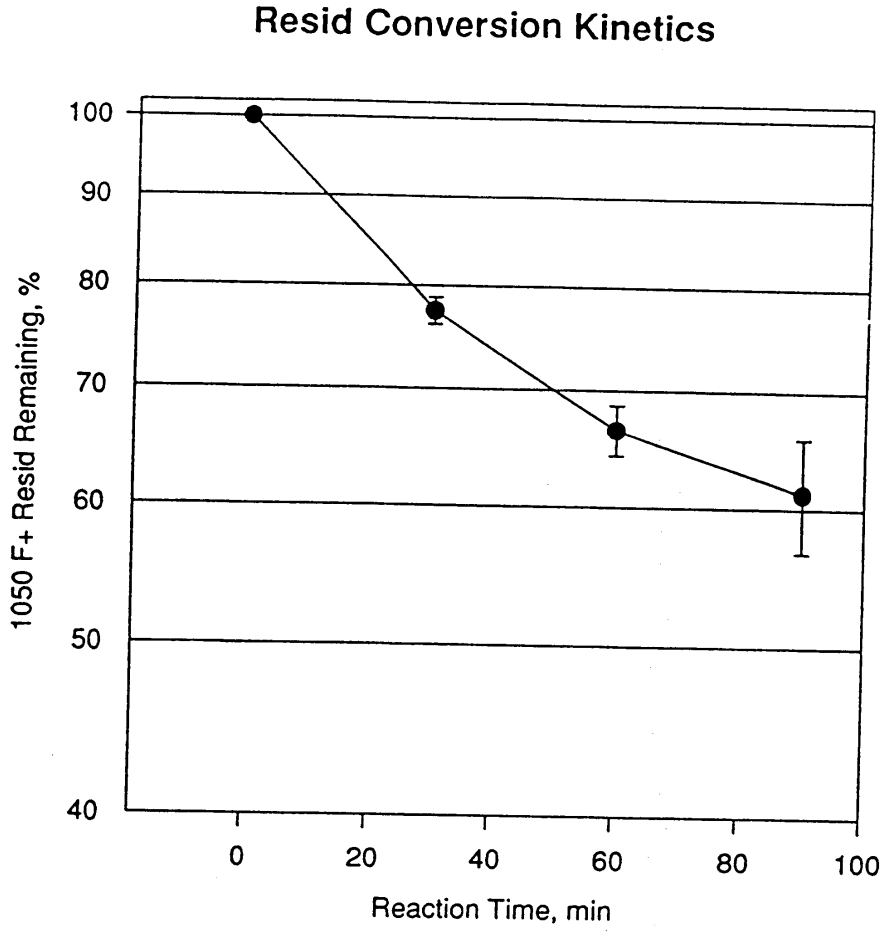



Figure 40. Disappearance of 566 °C$^+$ Resid vs Reaction Time for Hydrotreating Reactions at 440 °C, Without Pretreatment. (Cold charge pressure was 10.1 MPa hydrogen mixture containing 2% $H_2S$.)

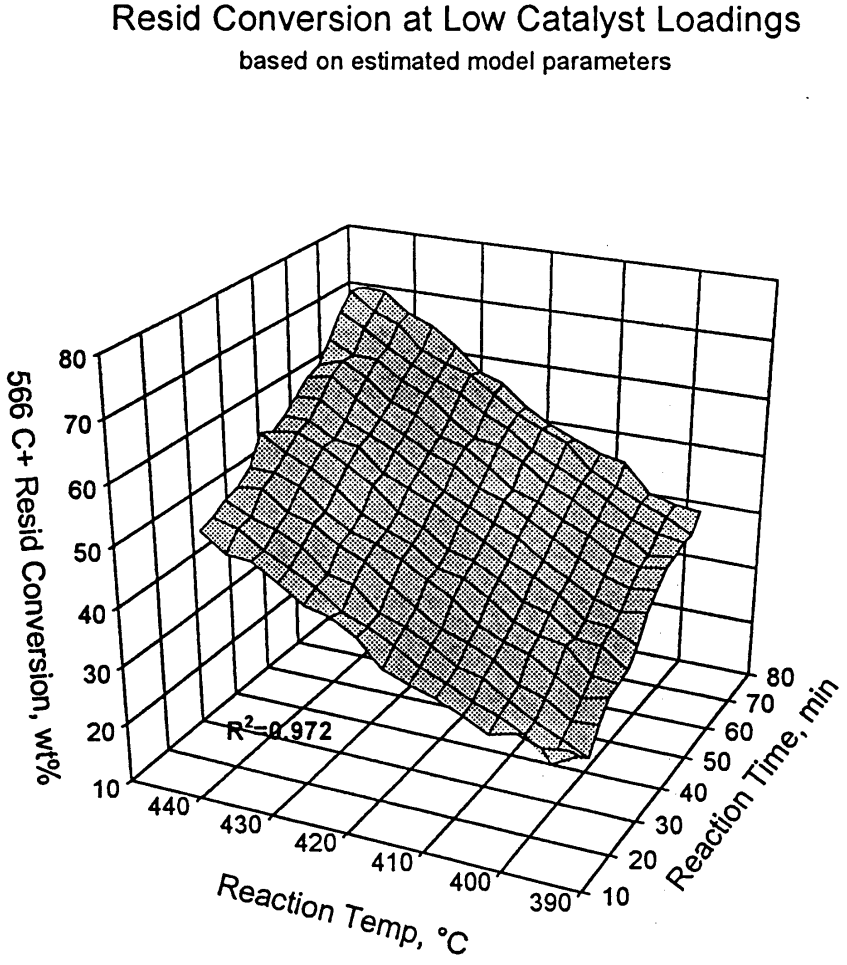



Figure 41. Resid Conversion vs Reaction Time and Temperature at Low Catalyst Loadings.

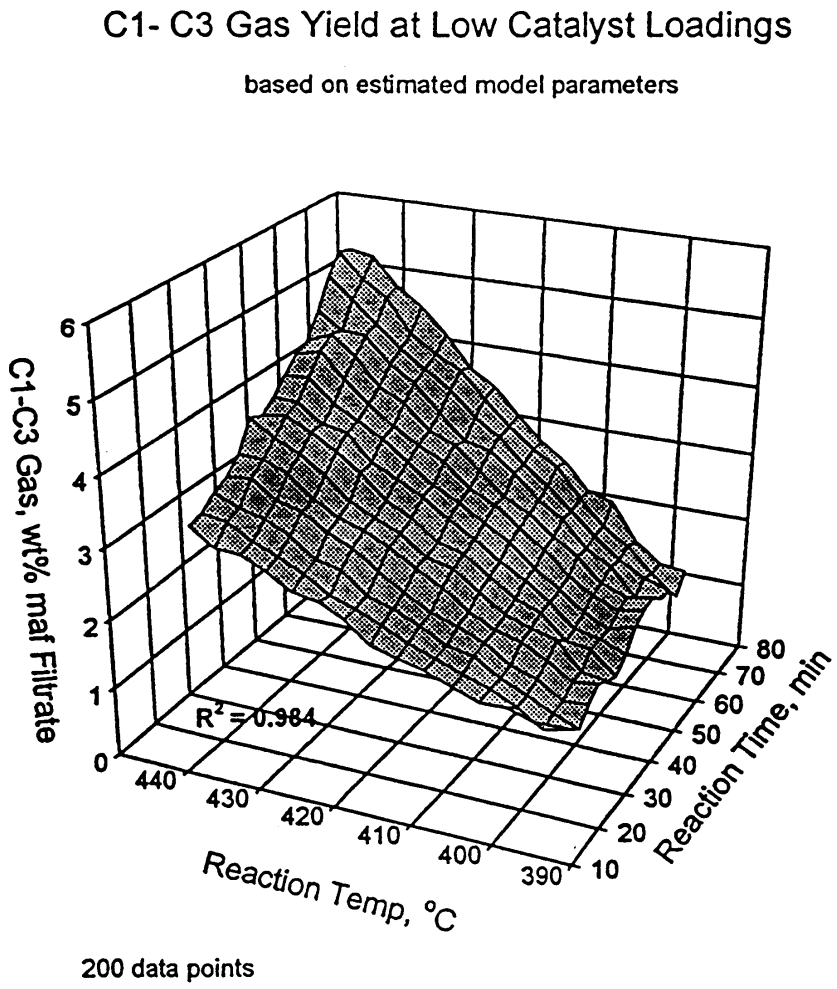



Figure 42. Hydrocarbon Gas Yield vs Reaction Time and Temperature at Low Catalyst Loadings.

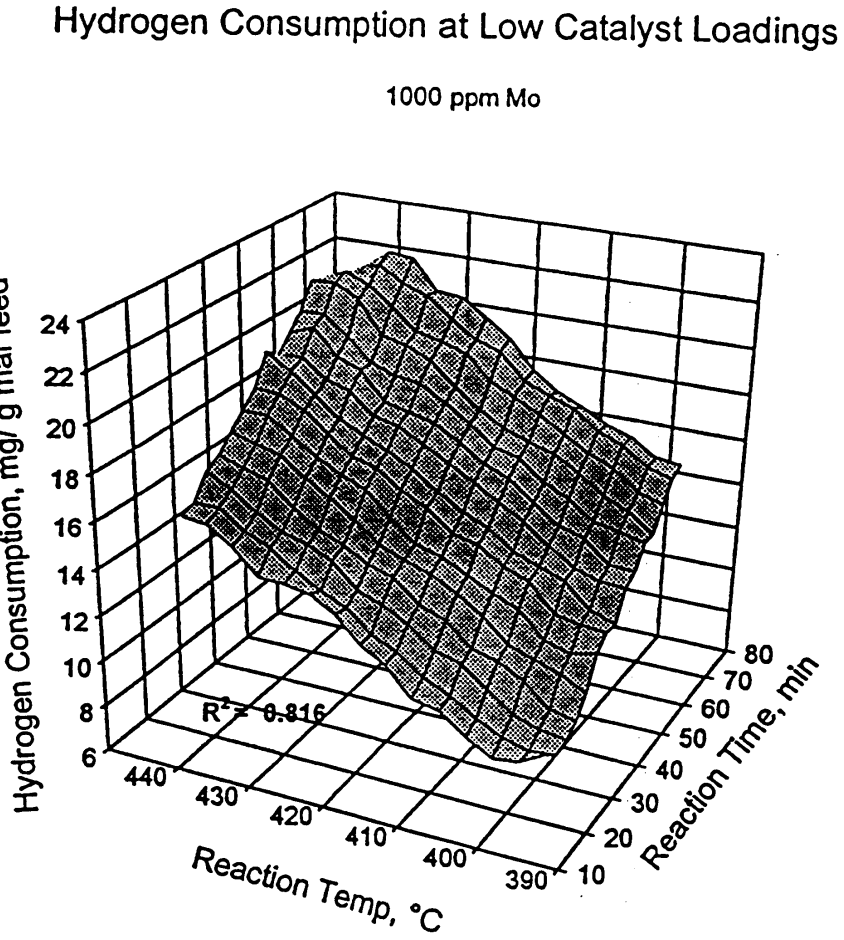



Figure 43. Hydrogen Consumption vs Reaction Time and Temperature at Low Catalyst Loadings.

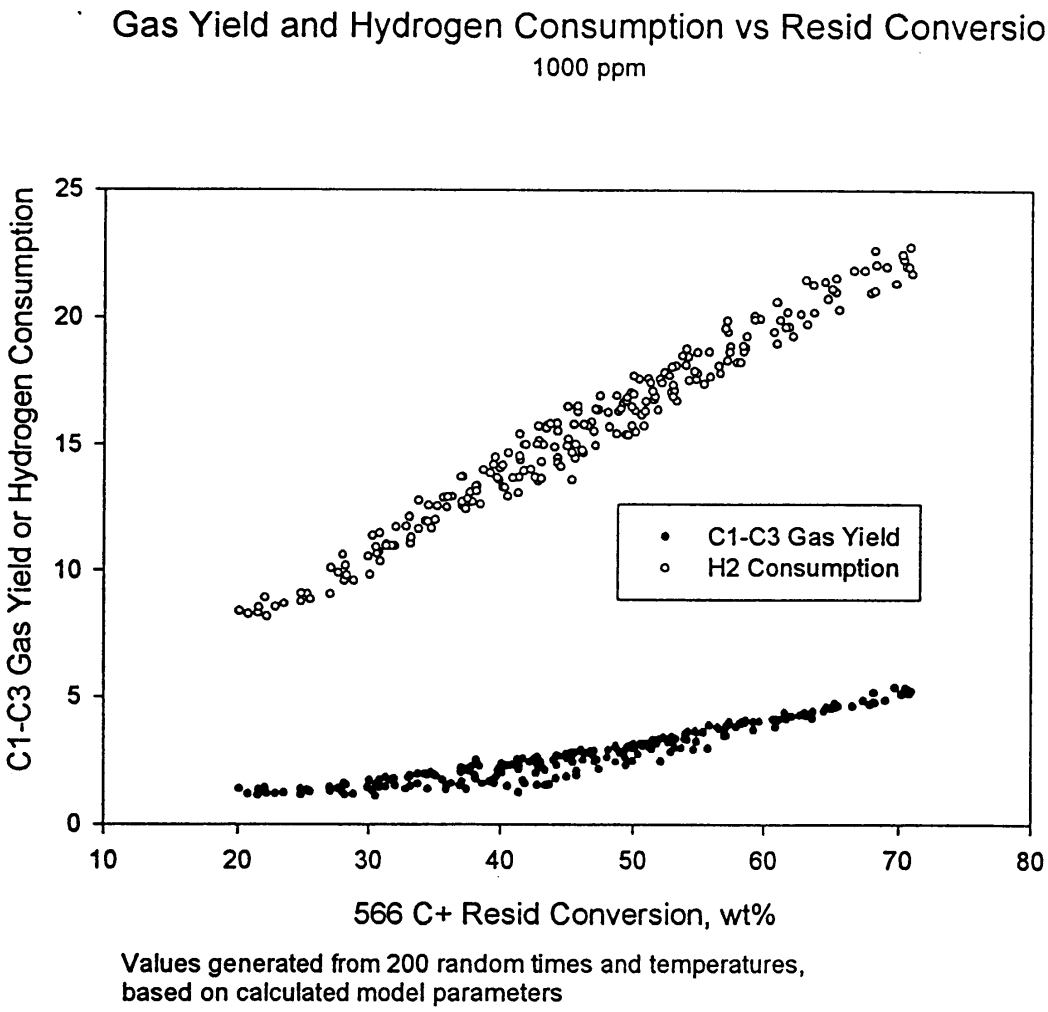



Figure 44. Gas Yield and Hydrogen Consumption vs Resid Conversion at Low Catalyst Loadings.

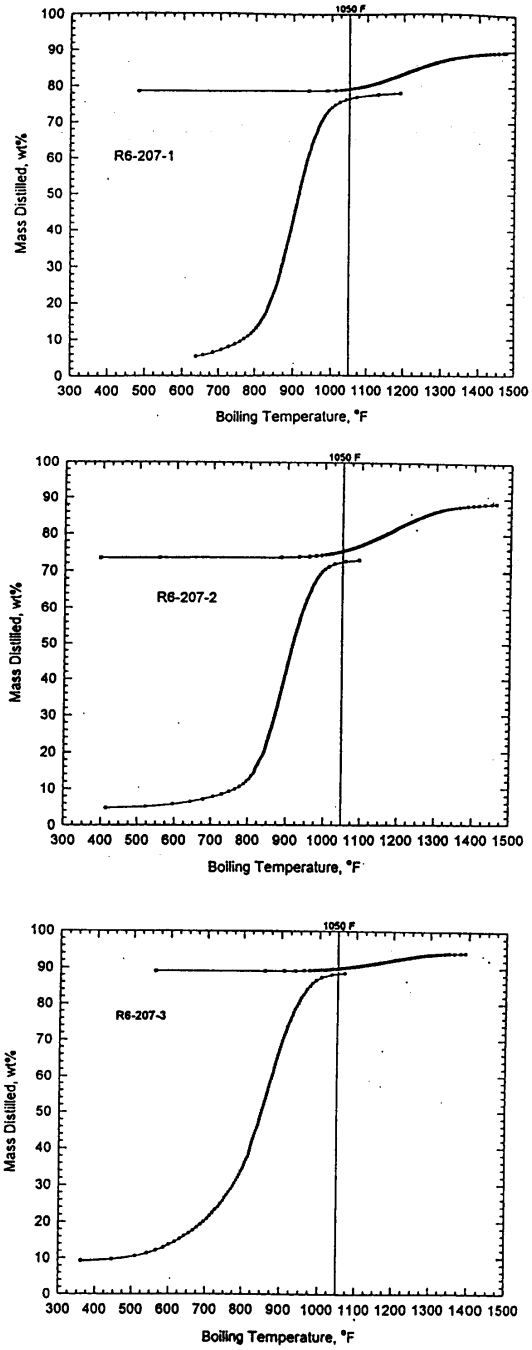



Figure 45. Simulated Distillation of Distillates and Resids for Parametric Study Experiments. (Two distillations are shown on each graph, matching the products of distillation for each experiment.)

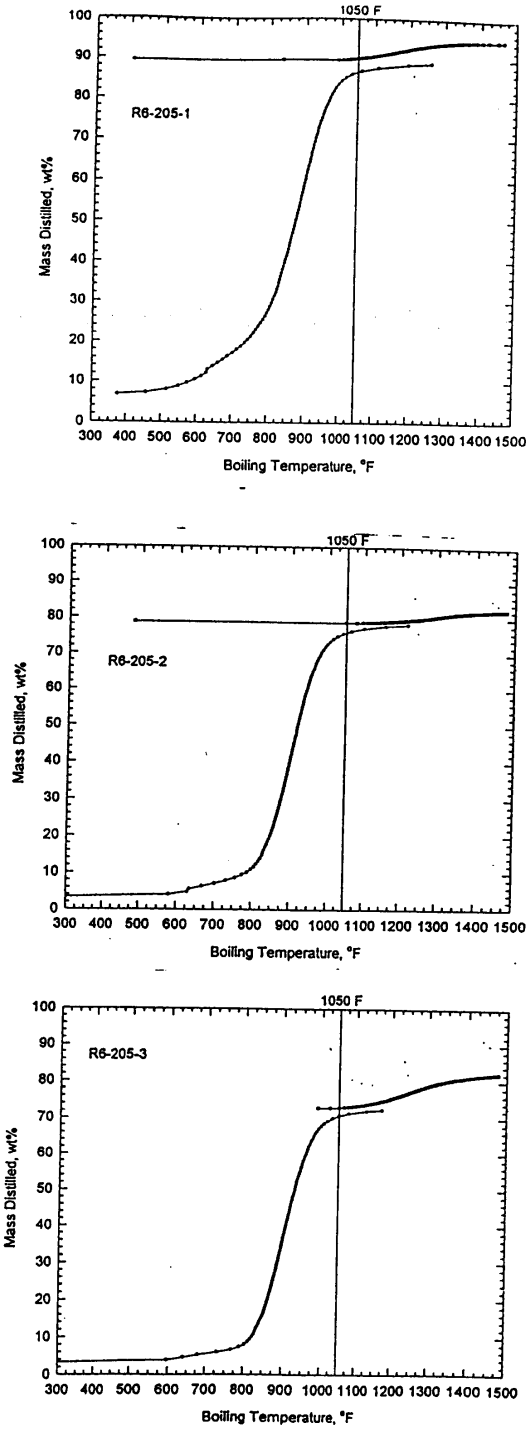



Figure 45B. Simulated Distillation of Distillates and Resids for Parametric Study Experiments. (Two distillations are shown on each graph, matching the products of distillation for each experiment.)

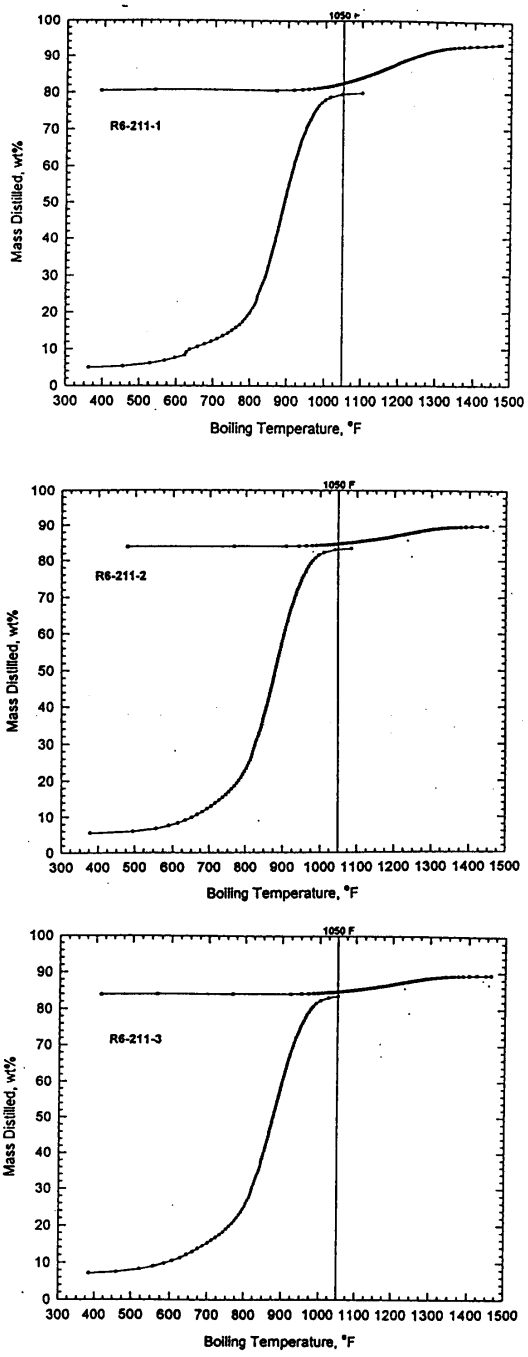



Figure 45C. Simulated Distillation of Distillates and Resids for Parametric Study Experiments. (Two distillations are shown on each graph, matching the products of distillation for each experiment.)

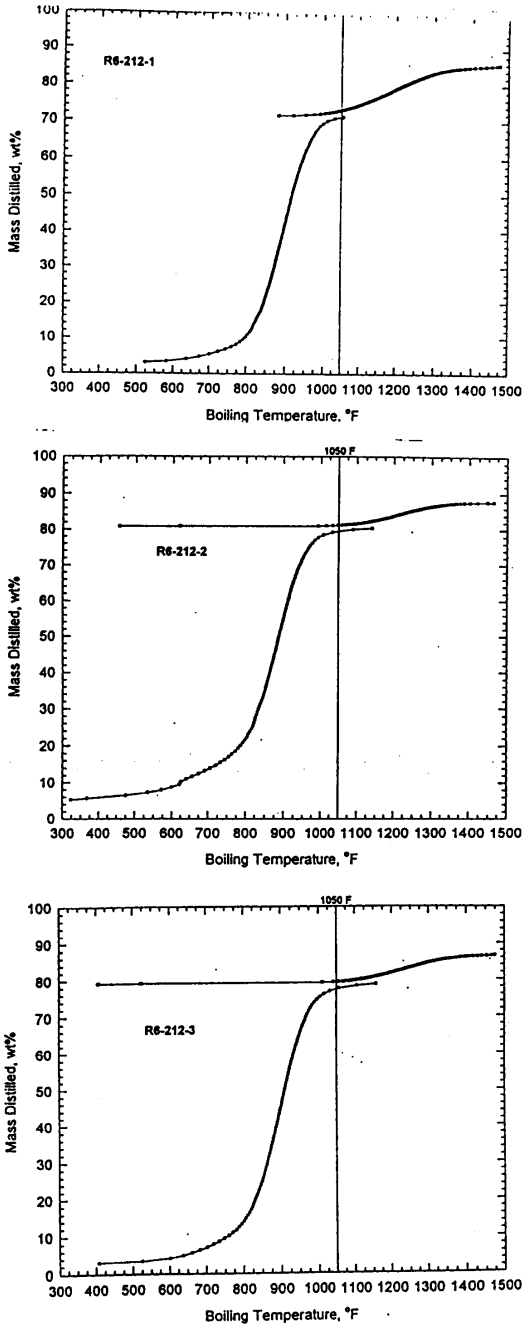



Figure 45D. Simulated Distillation of Distillates and Resids for Parametric Study Experiments. (Two distillations are shown on each graph, matching the products of distillation for each experiment.)

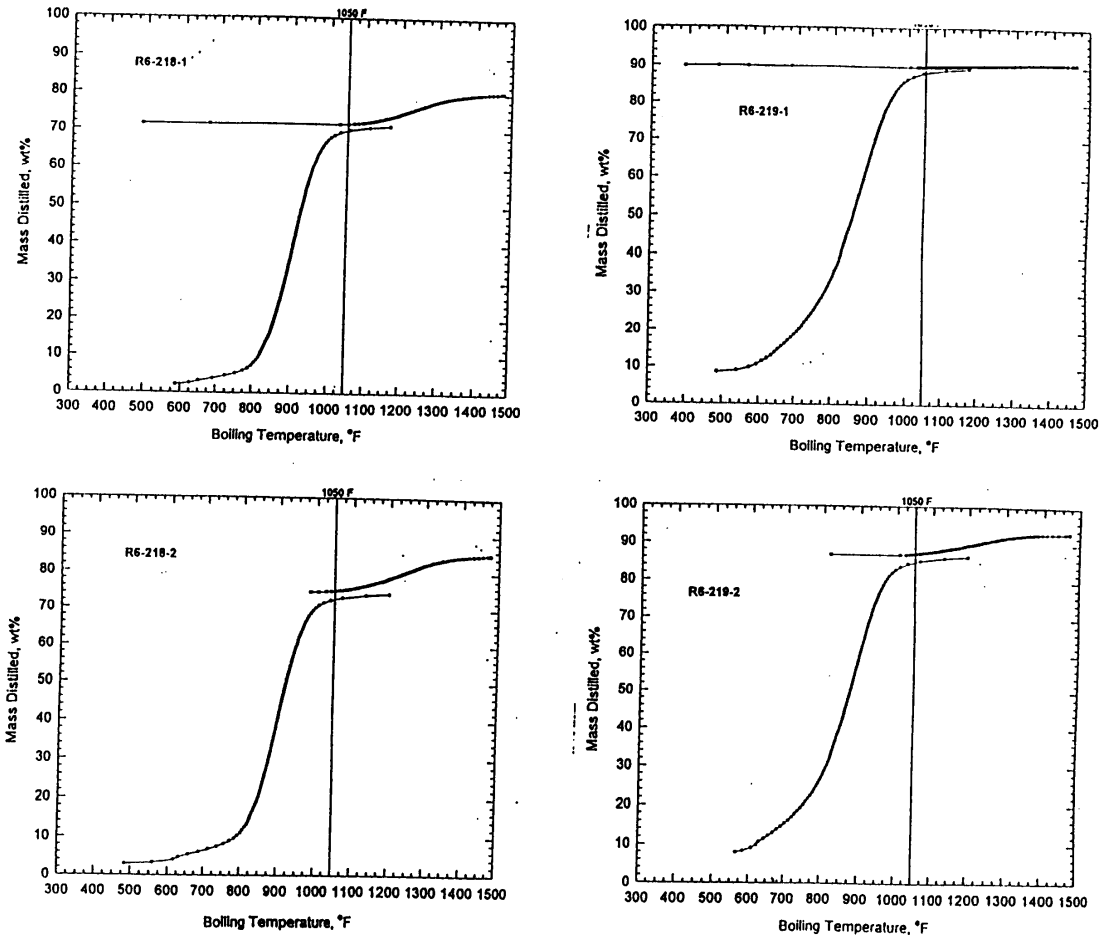



Figure 45E. Simulated Distillation of Distillates and Resids for Parametric Study Experiments. (Two distillations are shown on each graph, matching the products of distillation for each experiment.)

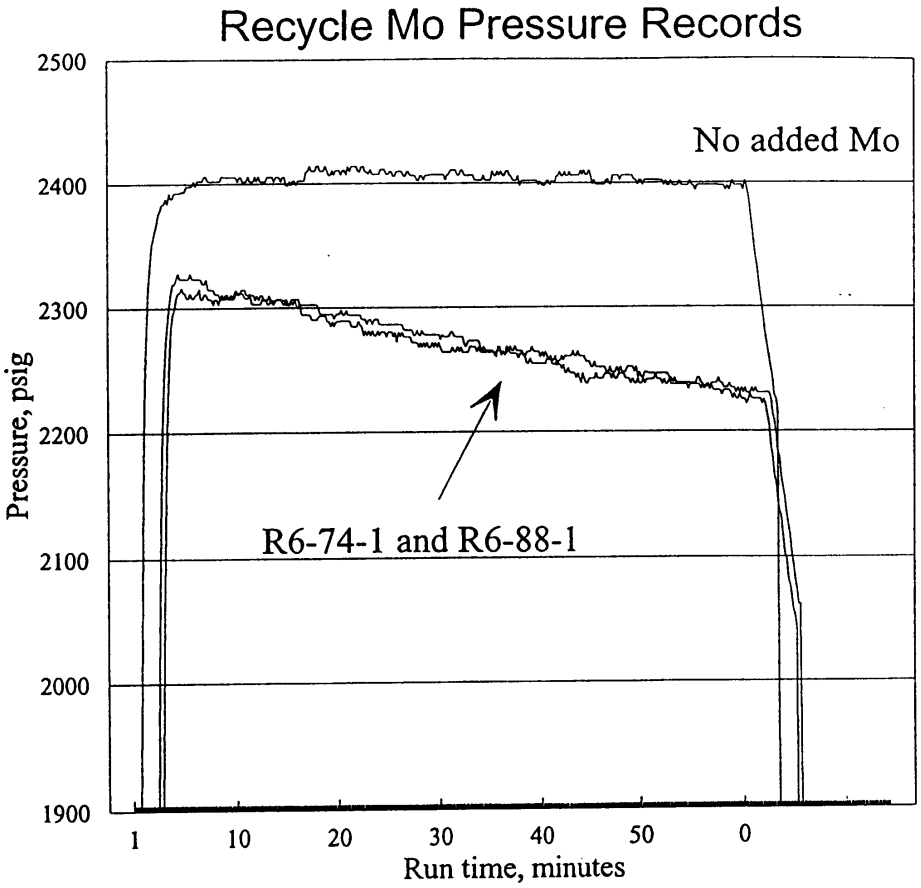



Figure 46. Pressure Record of First and Second Reactor Passes Using Molyvan L in Simulated Recycle.

# APPENDIX 1
## 45 mL MICROAUTOCLAVE TESTS

NORTH DAKOTA LIGNITE/HI"A" MICROAUTOCLAVE RUNS

Coteau Properties Co., FREEDOM Mine

| | | | CHARGE | | | | | | HI"A": | | | Coal Conv | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| RUN/DATE | Time (min) | Temp (°F) | Coal, g ND Lignite | Coal Moisture, % | Coal Ash, % | water, g | HI"A", g | Solvent g | dry Coal g:g | HI"A"/Hù mole/mole | Filter Cake g | wt % MAF Coal Basis | Comments |
| Run # 3a 9/12/95 | 45 | 572 | 10 | 28.4 | 4.46 | | 8 | 16 | 1.1 | 0.8 | - | - | Reactor overfilled, lost material on opening |
| Run # 3b 9/13/95 | 45 | 572 | 5 | 29.0 | 4.46 | | 4 | 8 | 1.1 | 0.8 | 2.8936 | 19.4 | very slow filtering |
| Run # 2a 9/18/95 | 60 | 662 | 4 | 27.9 | 4.46 | | 4 | 8 | 1.4 | 1.1 | 1.2992 | 57.5 | weight of THFinsols=sum of 3 filters |
| Run # 2b 9/19/95 | 60 | 662 | - | - | - | | - | - | | | - | - | lost valve, run aborted |
| Run # 4 10/02/95 | 45 | 662 | 5 | 28.1 | 4.46 | | 5 | 8 | 1.4 | 1.1 | 1.1149 | 72.2 | |
| Run # 7 10/03/95 | 45 | 662 | 5 | 28.9 | 4.46 | | 4 | 8*** | 1.1 | 0.8 | 1.0500 | 73.8 | |
| Run # 10 10/04/95 | 45 | 707 | 5 | 29.2 | 4.46 | | 4 | 8 | 1.1 | 0.8 | 0.7700 | 81.9 | |
| Run # 14 10/05/95 | 60 | 662 | 5 | 28.5 | 4.46 | | 8 | 5 | 2.2 | 1.7 | 0.7700 | 82.1 | |
| Run # 15 10/06/95 | 45 | 752 | 5 | 29.0 | 4.46 | | 0 | 8 | 0.0 | 0.0 | 1.2200 | 68.7 | |
| Run # 16 10/09/95 | 60 | 662 | 5 | 28.0 | 4.46 | | 7 | 5 | 1.9 | 1.5 | 0.8100 | 81.1 | |
| Run # 17 10/10/95 | 60 | 707 | 4.72 | 28.8 | 4.46 | | 4.72 | 7.55 | 1.4 | 1.0 | 0.5400 | 87.8 | |
| Run # 18 10/10/95 | 45 | 752 | 4.72 | 28.7 | 4.46 | | 4.72 | 7.55 | 1.4 | 1.0 | 0.4600 | 90.4 | |
| Run # 42b 11/21/95 | 60 | 662 | 3.79 | 28.6 | 4.46 | 1.16 | 6.00 | 6.06 | 2.2 | 0.8 | 0.6903 | 78.0 | |
| Run # 43b 11/21/95 | 60 | 662 | 3.51 | 28.6 | 4.46 | 2.34 | 5.54 | 5.62 | 2.2 | 0.5 | 0.8463 | 69.3 | |
| Run # 43c 11/29/95 | 45 | 662 | 3.51 | 28.6 | 4.46 | 2.34 | 5.54 | 5.62 | 2.2 | 0.5 | 0.7019 | 75.3 | |
| Run # 49 11/29/95 | 0 | 392-662 | 5 | 28.8 | 4.46 | | 4 | 8 | 1.1 | 0.8 | 2.4334 | 33.1 | |
| Run # 55 12/12/95 | 120 | 662 | 5 | 28.7 | 4.46 | | 4 | 8 | 1.1 | 0.8 | 0.7645 | 82.2 | |
| Run # 56 12/13/95 | 60 | 392-662 | 5 | 27.5 | 4.46 | | 4 | 8 | 1.1 | 0.9 | 0.9430 | 77.4 | Hold at 662F for 60min, check pres., filtered |
| Run # 60 12/19/95 | 150 | 707 | 5 | 27.4 | 4.46 | | 4 | 8 | 1.1 | 0.9 | 0.4265 | 92.4 | |
| Run # 62 01/04/96 | 60 | 662 | 5 | 28.4 | 4.46 | | 4 | 8 | 1.1 | 0.8 | 1.0374 | 74.3 | 0.017g Na F in water solution added to lignite, dried before run |
| Run # 65 01/08/96 | 30 | 662 | 5 | 27.6 | 4.46 | | 4 | 8 | 1.1 | 0.9 | 1.6100 | 58.1 | 0.05g Na F in water solution added to lignite, dried before run |
| Run # 67 01/08/96 | 60 | 662 | 5 | 27.6 | 4.46 | | 4 | 8 | 1.1 | 0.9 | 1.0400 | 74.6 | 0.05g Na F in water solution added to lignite, dried before run |
| Run # 68 01/09/96 | 60 | 662 | 5 | 27.6 | 4.46 | | - | 8 | 0.0 | 0.0 | N/A | 77.1 | 4.5g Na F as dry crystals added to lignite, dried before run, conver,based on THF sols. |
| Run # 69 01/10/96 | 60 | 662 | 5 | 26.2 | 4.46 | | - | 8 | 0.0 | 0.0 | 1.0386 | 75.2 | 4.5g Na F in water sotution added to lignite, dried before run |
| Run # 70 01/11/96 | 60 | 662 | 5 | 11.3 | 11.42 | | 4 | 8 | 0.9 | 2.1 | 1.9346 | 63.6 | High Na lignite, pres. checked, filtered |
| Run # 71 01/15/96 | 60 | 662 | 5 | 28.4 | 4.46 | | - | 8 | 0.0 | 0.0 | 0.9951 | 75.6 | 4.5g Na F in water added to lignite, dried before run, isols washed with H2O |
| Run # 72 01/15/96 | 60 | 662 | 5 | 28.4 | 4.46 | | - | 8 | 0.0 | 0.0 | 1.0104 | 75.1 | 4.5g Na F in water added to lignite, dried before run, isols washed with H2O |
| Run # 85 02/22/96 | 60 | 662 | 4.50 | 11.8 | 11.42 | | 4.38 | 8.76 | 1.1 | 2.5 | 1.7159 | 64.1 | High Na lignite, pressure checked, filtered |
| Run # 86 02/22/96 | 45 | 662 | 4.50 | 11.8 | 11.42 | | 4.38 | 8.76 | 1.1 | 2.5 | 1.9637 | 57.0 | High Na lignite, pressure checked, filtered |
| Run # 87 02/26/96 | 45 | 707 | 4.50 | 12.0 | 11.42 | | 4.38 | 8.76 | 1.1 | 2.4 | 1.2708 | 76.7 | High Na lignite, Pressure checked, filtered |
| Run # 88 02/23/96 | 45 | 662 | 5 | 29.0 | 4.46 | | 4 | 8 | 1.1 | 0.8 | 1.2952 | 66.5 | Low Na lignite, pressure checked, filtered |
| Run # 89b 02/29/96 | 150 | 662 | 5 | 29.6 | 4.46 | | 4 | 8 | 1.1 | 0.8 | 0.6218 | 86.2 | Low Na lignite, pressure checked, filtered, .02g moist. on MgO2 trap |
| Run # 90c 03/01/96 | 150 | 752 | 5 | 28.6 | 4.46 | | 4 | 8 | 1.1 | 0.8 | 0.4528 | 91.4 | Low Na lignite, pressure checked, filtered, .02g moist. on MgO2 trap |
| Run # 93 03/14/96 | 60 | 662 | 6.25 | 32.2 | 4.46 | | 6.25 | 10.0 | 1.5 | 0.9 | 1.1186 | 77.0 | 60mesh lignite, high moist., press.checked, filtered |
| Run # 99 03/26/96 | 60 | 662 | 4.71 | 11.4 | 11.42 | 1.54 | 6.25 | 10.0 | 1.5 | 0.9 | 1.0960 | 83.2 | High Na lignite, press. check, filtered |
| Run # 100 03/27/96 | 60 | 662 | 4.71 | 11.8 | 11.42 | 1.54 | 6.25 | 10.0 | 1.5 | 0.9 | 1.1248 | 82.3 | High Na lignite, press. check, filtered |
| Run # 101 03/27/96 | 60 | 662 | 5.15 | 11.8 | 11.42 | 1.75 | 4.59 | 11.01 | 1.0 | 0.6 | 1.5620 | 74.1 | High Na lignite, press. check, filtered |

Run # 69... Coal conversion based on water washed THF insolubles

Run # 68...Coal conversion based on THF solubles

# APPENDIX 1
## 45 mL MICROAUTOCLAVE TESTS

BLACK THUNDER/HI"A" MICROAUTOCLAVE RUNS

| | | | CHARGE | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| RUN/DATE | Time (min) | Temp (°F) | Coal, g Black Thunder | Coal Moisture, % | Coal Ash, % | water, g | HI"A", g | Solvent g | HI"A": Dry Coal g:g | solvent: dry coal g:g | HI"A"/Hùd2 mole/mole | Filter Cake, g | Coal Conv wt % MAF Coal Basis | Comments |
| Run # 20 10/17/95 | 45 | 752 | 5 | 18.1 | 5.54 | | 4 | 8 | 1.0 | 2.0 | 1.3 | 0.7000 | 87.8 | |
| Run # 21 10/17/95 | 45 | 707 | 5 | 21.2 | 5.54 | | 4 | 8 | 1.0 | 2.0 | 1.1 | 0.9600 | 80.1 | |
| Run # 22 10/18/95 | 45 | 662 | 5 | 20.5 | 5.54 | | 4 | 8 | 1.0 | 2.0 | 1.2 | 1.6146 | 62.9 | |
| Run # 34 11/1/95 | 45 | 752 | 3.90 | 17.8 | 5.54 | 0.56 | 5.36 | 7.15 | 1.7 | 2.2 | 1.3 | 0.4645 | 90.5 | |
| Run # 35 11/8/95 | 45 | 752 | 3.35 | 21.6 | 5.54 | 1.12 | 5.36 | 7.15 | 2.0 | 2.7 | 0.9 | 0.3598 | 91.4 | |
| Run # 36 11/9/95 | 45 | 662 | 3.70 | 21.6 | 5.54 | | 9.25 | 5.90 | 3.2 | 2.0 | 3.5 | 0.6772 | 81.2 | |
| Run # 37 11/13/95 | 45 | 662 | 1.70 | 21.8 | 5.54 | 2.00 | 9.25 | 5.90 | 7.0 | 4.4 | 1.2 | 0.2182 | 88.5 | |
| Run # 38c 11/15/95 | 45 | 662 | 3.70 | 22.1 | 5.54 | | 7.40 | 3.70 | 2.6 | 1.3 | 2.7 | 0.8037 | 76.3 | |
| Run # 39b 11/16/95 | 45 | 662 | 6.53 | 18.2 | 5.54 | | 0.00 | 10.47 | 0.0 | 2.0 | 0.0 | 3.4961 | 36.6 | |
| Run # 40 11/16/95 | 45 | 707 | 6.53 | 19.8 | 5.54 | | 0.00 | 10.47 | 0.0 | 2.0 | 0.0 | 2.7473 | 50.3 | |
| Run # 41 11/16/95 | 45 | 752 | 6.53 | 19.4 | 5.54 | | 0.00 | 10.47 | 0.0 | 2.0 | 0.0 | 1.7828 | 70.0 | |
| Run # 46 11/27/95 | 45 | 662 | 2.87 | 21.0 | 5.54 | 2.18 | 7.35 | 5.92 | 3.2 | 2.6 | 0.8 | 0.5592 | 79.8 | |
| Run # 47 11/28/95 | 15 | 662 | 5 | 21.8 | 5.54 | | 4 | 8 | 1.0 | 2.0 | 1.1 | 2.1977 | 46.4 | |
| Run # 48 11/28/95 | 90 | 662 | 5 | 21.8 | 5.54 | | 4 | 8 | 1.0 | 2.0 | 1.1 | 1.1325 | 75.2 | |
| Run # 51 11/30/95 | 0 | 392-662 | 5 | 18.6 | 5.54 | | 4 | 8 | 1.0 | 2.0 | 1.3 | 2.3087 | 45.8 | |
| Run # 58 12/14/95 | 90 | 707 | 5 | 22.2 | 5.54 | | 4 | 8 | 1.0 | 2.1 | 1.1 | 0.6487 | 88.2 | |
| Run # 59 12/18/95 | 120 | 707 | 5 | 22.6 | 5.54 | | 4 | 8 | 1.0 | 2.1 | 1.1 | 0.5960 | 89.6 | |
| Run # 57 01/03/96 | 45 | 392-662 | 5 | 21.7 | 5.54 | | 4 | 8 | 1.0 | 2.0 | 1.1 | 1.4574 | 66.5 | Heat from 392 to 662 and hold for 45 min. |
| Run # 75 01/23/96 | 150 | 752 | 5 | 20.0 | 5.54 | | 4 | 8 | 1.0 | 2.0 | 1.2 | 0.7313 | 86.5 | |
| Run # 74B 01/29/96 | 45 | 752 | 5 | 22.4 | 5.54 | | 4 | 8 | 1.0 | 2.1 | 1.1 | 0.6250 | 88.8 | Pres. check, distill H2O, filter, distill THF SOLS. |
| Run # 76 02/05/96 | 150 | 707 | 5 | 21.0 | 5.54 | | 4 | 8 | 1.0 | 2.0 | 1.1 | 0.6017 | 89.7 | Pres. check, distill H2O, filter, distill THF SOLS.,150min run |
| Run # 76B 02/15/96 | 150 | 707 | 5 | 21.6 | 5.54 | | 4 | 8 | 1.0 | 2.0 | 1.1 | 0.5686 | 90.4 | Pres. check, distill H2O, filter, distill THF SOLS., repeat of Run 76 |
| Run # 91 02/27/96 | 15 | 707 | 5 | 22.3 | 5.54 | | 4 | 8 | 1.0 | 2.1 | 1.1 | 1.5852 | 62.7 | |
| Run # 92 02/27/96 | 15 | 752 | 5 | 22.3 | 5.54 | | 4 | 8 | 1.0 | 2.1 | 1.1 | 0.9626 | 79.6 | |
| Run # 95 03/19/96 | 90 | 707 | 5 | 21.1 | 5.54 | | 4 | 8 | 1.0 | 2.0 | 1.1 | 0.6800 | 87.6 | |
| Run # 102b 04/01/96 | 60 | 662 | 5.37 | 21.1 | 5.54 | 0.88 | 6.25 | 10.0 | 1.5 | 2.4 | 0.9 | 0.9786 | 81.4 | Wilsonville Run 262 E V1074 whole oil |
| Run # 103 04/01/96 | 60 | 662 | 5.37 | 21.7 | 5.54 | 0.88 | 4.20 | 12.05 | 1.0 | 2.9 | 0.6 | 1.2320 | 74.8 | Wilsonville Run 262 E V1074 whole oil |
| Run # 106 04/03/96 | 60 | 662 | 5.37 | 22.1 | 5.54 | 0.88 | 6.25 | 15.0 | 1.5 | 3.6 | 0.9 | 0.9520 | 81.8 | Wilsonville Run 262 E V1074 whole oil |
| Run # 108 04/04/96 | 60 | 662 | 9.50 | 21.9 | 5.54 | | 7.40 | 18.4 | 1.0 | 2.5 | 1.1 | 2.1075 | 75.8 | Total load = 35.3g. whole oil |
| Run # 109 04/15/96 | 60 | 662 | 5.37 | 21.8 | 5.54 | 0.88 | 4.18 | 15.0 | 1.0 | 3.6 | 0.6 | 1.2150 | 75.2 | |
| Run # 110 04/16/96 | 60 | 662 | 4.17 | 21.8 | 5.54 | 0.68 | 4.86 | 7.77 | 1.5 | 2.4 | 0.9 | 0.8763 | 77.4 | Wilsonville Run 262 E V1074 whole oil |
| Run # 118B (5/3/96) | 60 | 662 | 3.60 | 0.9 | 5.54 | | 5.35 | 8.55 | 1.5 | 2.4 | 49.5 | 1.5121 | 61.0 | "weathered coal"(moist.<1.0%), whole oil |
| Run # 119 (5/6/96) | 60 | 662 | 4.48 | 0.9 | 5.54 | | 6.88 | 11.00 | 1.5 | 2.5 | 51.2 | 1.6663 | 66.1 | "weathered coal"(moist.<1.0%), whole oil |
| Run #133 (7/2/96) | 60 | 662 | 5.00 | 22.5 | 5.54 | | 4.00 | 8.00 | 1.0 | 2.1 | | 1.4554 | 66.1 | Wilsonville Run 262 E V1074 whole oil |
| Run # 134 (7/2/96) | 60 | 662 | 4.47 | 22.5 | 5.54 | | 5.36 | 7.15 | 1.5 | 2.1 | | 1.0599 | 73.8 | Wilsonville Run 262 E V1074 whole oil |
| Run # 74c (8/13/96) | 45 | 752 | 5.00 | 21.1 | 5.54 | | 4.00 | 8.00 | 1.0 | 2.0 | | 0.6951 | 87.2 | |
| Run # 73c (8/14/96) | 150 | 662 | 5.00 | 21.0 | 5.54 | | 4.00 | 8.00 | 1.0 | 2.0 | | 0.9231 | 81.1 | |
| Run # 76c (8/14/96) | 150 | 707 | 5.00 | 21.0 | 5.54 | | 4.00 | 8.00 | 1.0 | 2.0 | | 0.6496 | 88.4 | |

# APPENDIX 1
# 45 mL MICROAUTOCLAVE TESTS

BLACK THUNDER/HI"B" MICROAUTOCLAVE RUNS

| RUN/DATE | Time (min) | Temp. (° F) | CHARGE | | | | | Filter Cake g | Coal Conv. wt % MAF Coal Basis | COMMENTS |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Coal, g Black Thunder | Coal Moisture, | Coal Ash, % | HI"B" g | Solvent g | | | |
| Run # 31 10/30/95 | 45 | 752 | 5 | 18.9 | 5.54 | 4 | 8 | 1.3675 | 70.2 | wash THF insols. with warm dist. water, filt |
| Run # 32 10/31/95 | 45 | 662 | 5 | 17.9 | 5.54 | 4 | 8 | 1.2934 | 72.5 | wash THF insols. with warm dist. water, filt |
| Run # 33 11/01/95 | 45 | 662 | 4.25 | 19.4 | 5.54 | 5.95 | 6.80 | 2.8634 | 17.4 | value suspect |
| | | | | | | | | | | |
| | | | | | | | | | | |
| | | | | | | | | | | |

# APPENDIX 1
# 45 mL MICROAUTOCLAVE TESTS

GLENHAROLD LIGNITE/ HI"A" MICROAUTOCLAVE RUNS

| | | | CHARGE | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| RUN/DATE | Time (min) | Temp (°F) | Coal, g Glenharold Lignite | Lignite Moisture, % | Lignite Ash, % | Water g | HI"A" g | Solvent g | HI"A" dry coal g:g | Solvent Dry Coal g:g | HI"A"/H2O mole/mole | Filter Cake, g | Coal Conv. wt % MAF Coal Basis | Comments |
| Run # 77 02/07/96 | 45 | 662 | 5 | 11.6 | 9.48 | | 4 | 8 | 0.9 | 1.8 | 2.1 | 2.8742 | 38.6 | |
| Run # 78 02/08/96 | 45 | 752 | 5 | 11.6 | 9.48 | | 4 | 8 | 0.9 | 1.8 | 2.1 | 0.7411 | 91.9 | |
| Run # 79 02/13/96 | 45 | 707 | 5 | 11.6 | 9.48 | | 4 | 8 | 0.9 | 1.8 | 2.1 | 1.0025 | 85.4 | |
| | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | |
| Run # 97 03/25/96 | 60 | 662 | 4.71 | 11.6 | 9.48 | 1.54 | 4.20 | 12.05 | 1.0 | 2.9 | 0.6 | 0.7935 | 89.4 | Wilsonville Run 262E V1074 whole oil |
| Run# 98 03/26/96 | 60 | 662 | 5.15 | 11.6 | 9.48 | 1.75 | 4.59 | 11.01 | 1.0 | 2.4 | 0.6 | 0.8391 | 90.1 | |
| Run # 120 05/07/96 | 60 | 662 | 4.50 | 11.6 | 9.48 | | 4.38 | 8.76 | 1.1 | 2.2 | 2.5 | 1.3884 | 71.9 | 950psig N2 added, pressure tested, filtered, whole oil V1074 |
| Run #127 (6/696) | 60 | 662 | 5.12 | 11.60 | 9.48 | 1.72 | 4.61 | 11.03 | 1.0 | 2.4 | 0.6 | 0.8472 | 89.8 | |
| Run #127b (6/26/96) | 60 | 662 | 5.15 | 11.00 | 9.48 | 1.75 | 4.59 | 11.01 | 1.0 | 2.4 | 0.6 | 0.8323 | 90.4 | |
| Run #131 (7/1/96) | 60 | 662 | 4.50 | 11.60 | 9.48 | | 4.38 | 8.76 | 1.1 | 2.2 | 2.5 | 1.2801 | 74.9 | |
| Run #132 (7/1/96) | 60 | 662 | 4.50 | 11.60 | 9.48 | | 6.00 | 7.55 | 1.5 | 1.9 | 3.4 | 1.1224 | 79.3 | |
| Run #144 (7/19/96) | 60 | 662 | 5.64 | 11.60 | 9.48 | 1.89 | 4.98 | 9.97 | 1.0 | 2.0 | 0.6 | 1.0814 | 86.5 | |
| Run #145 (7/22/96) | 60 | 662 | 5.64 | 12.10 | 9.48 | 1.89 | 4.98 | 9.97 | 1.0 | 2.0 | 0.6 | 0.7804 | 93.1 | Lummus 3LCF7 pasting solvent distillate |
| Run #146 (7/22/96) | 60 | 662 | 5.90 | 12.10 | 9.48 | 1.98 | 5.22 | 9.40 | 1.0 | 1.8 | 0.6 | 1.2382 | 84.1 | |
| Run #147 (7/23/96) | 60 | 662 | 6.34 | 10.20 | 9.48 | 2.15 | 5.60 | 8.40 | 1.0 | 1.5 | 0.6 | 0.8643 | 93.7 | Lummus 3LCF7 pasting solvent distillate |
| Run #127c (8/15/96) | 60 | 662 | 5.15 | 12.50 | 9.48 | 1.75 | 4.59 | 11.01 | 1.0 | 2.4 | 0.6 | 1.1323 | 82.7 | Run 8-LA recycle solvent |
| Run #127d (8/16/96) | 60 | 662 | 5.15 | 12.50 | 9.48 | 1.75 | 4.98 | 11.01 | 1.1 | 2.4 | 0.6 | 1.2364 | 80.2 | Run 8-LA recycle solvent |
| Run #159 (9/5/96) | 60 | 662 | 5.64 | 12.50 | 9.48 | 1.89 | 4.98 | 8.40 | 1.0 | 1.7 | 0.6 | | 91.0 | Kawasaki Anthracene Oil |
| Run #160 (9/9/96) | 60 | 662 | 5.64 | 12.50 | 9.48 | 1.89 | 4.98 | 8.40 | 1.0 | 1.7 | 0.6 | | 93.0 | Reilly Anthracene Oil |

# APPENDIX 1
# 45 mL MICROAUTOCLAVE TESTS

OHIO 11 MINE/HI"A" MICROAUTOCLAVE RUNS

| | | | CHARGE | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| RUN/DATE | Time (min) | Temp ( °F) | Coal, g Ohio 11 Bituminous | Coal Moisture, % | Coal Ash, % | Water, g | HI"A" g | Solvent g | HI"A": dry coal g:g | Solvent Dry Coal g:g | HI"A"/Hùc mole/mole | Filter Cake, g | Coal Conv. wt % MAF Coal Basis | Comments |
| RUN # 104 04/03/96 | 60 | 662 | 5.0 | 2.8 | 6.71 | | 4.75 | 7.25 | 1.0 | 1.5 | 10.2 | 0.8338 | 88.8 | Wilsonville Run 262E V1074 Distillate |
| RUN # 105 04/03/96 | 60 | 662 | 4.39 | 2.8 | 6.71 | 1.86 | 4.19 | 12.06 | 1.0 | 2.8 | 0.6 | 0.6420 | 91.1 | Wilsonville Run 262E V1074 Distillate |
| RUN # 107 04/04/96 | 60 | 662 | 6.00 | 2.8 | 6.71 | | 2.90 | 8.10 | 0.5 | 1.4 | 5.2 | 2.0352 | 69.8 | Wilsonville Run 262E V1074 Distillate |
| RUN # 111 04/09/96 | 60 | 662 | 5.00 | 2.8 | 6.71 | | 4.85 | 7.15 | 1.0 | 1.5 | 10.4 | 0.7810 | 90.0 | Wilsonville Run 262E V1074 Distillate |
| RUN # 114 04/11/96 | 60 | 707 | 6.00 | 2.8 | 6.71 | | 2.90 | 8.10 | 0.5 | 1.4 | 5.2 | 1.0040 | 88.7 | Wilsonville Run 262E V1074 Distillate |
| RUN # 115 04/11/96 | 60 | 662 | 4.39 | 2.8 | 6.71 | | 6.28 | 9.96 | 1.5 | 2.3 | 15.3 | 1.7566 | 63.1 | Wilsonville Run 262E V1074 Whole Oil |
| RUN # 116 04/12/96 | 60 | 752 | 5.00 | 2.8 | 6.71 | | 4.85 | 7.15 | 1.0 | 1.5 | 10.4 | 0.6266 | 93.4 | Wilsonville Run 262E V1074 Whole Oil |
| RUN # 117 04/15/96 | 60 | 662 | 5.00 | 2.8 | 6.71 | | 4.85 | 7.15 | 1.0 | 1.5 | 10.4 | 0.9305 | 86.7 | Wilsonville Run 262E V1074 Whole Oil |
| Run # 122B 05/08/96 | 60 | 572 | 5.00 | 2.8 | 6.71 | | 4.85 | 7.15 | 1.0 | 1.5 | 10.4 | 3.1295 | 38.2 | Wilsonville Run 262E V1074 Whole Oil |
| Run # 125B 05/17/96 | 60 | 662 | 5.00 | 2.8 | 6.88 | | - | 8.00 | 0.0 | 1.6 | 0.0 | 2.8291 | 44.9 | Wilsonville Run 262E V1074 Whole Oil |
| Run # 126 05/16/96 | 60 | 752 | 5.00 | 2.8 | 6.88 | | - | 8.00 | 0.0 | 1.6 | 0.0 | 1.5878 | 72.3 | Wilsonville Run 262E V1074 Whole Oil |

# APPENDIX 1
## 45 mL MICROAUTOCLAVE TESTS
## MICROAUTOCLAVE TESTS WITH CO/Hùd2ù0dO; CO/METHANOL/Hùd2ù0dO

| RUN/DATE/COAL | Time (min) | Temp (°F) | Coal g | Coal Moisture, % | Coal Ash, % | Water, g | Methanol, g | CO psi, cold | Solvent g | Solvent: Dry Coal g:g | Filter Cake, g | Coal Conv. wt % MAF Coal Basis |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Black Thunder Mine Subbituminous Coal | | | | | | | | | | | | |
| Run# 135 7/8/96 | 60 | 662 | 7.00 | 22.5 | 5.54 | - | | 150 | 6.40 | 1.2 | 3.9609 | 28.6 |
| Run# 136 7/8/96 | 60 | 662 | 7.00 | 22.5 | 5.54 | - | | 500 | 6.40 | 1.2 | 3.7227 | 33.2 |
| Run# 137 7/9/96 | 60 | 662 | 7.00 | 22.3 | 5.54 | - | | 750 | 6.40 | 1.2 | 3.4793 | 38.1 |
| Run# 138 7/9/96 | 60 | 662 | 7.00 | 22.5 | 5.54 | - | | 1000 | 6.40 | 1.2 | 3.4462 | 38.8 |
| Run# 139 7/10/96 | 30 | 662 | 7.00 | 22.5 | 5.54 | - | | 1000 | 6.40 | 1.2 | 5.1637 | 5.1 |
| Run# 140 7/10/96 | 45 | 662 | 7.00 | 22.3 | 5.54 | - | | 1000 | 6.40 | 1.2 | 3.8562 | 30.6 |
| Run# 140B 7/10/96 | 45 | 662 | 7.00 | 21.5 | 5.54 | - | | 1000 | 6.40 | 1.2 | 3.4530 | 39.0 |
| Run# 141 7/11/96 | 90 | 662 | 7.00 | 21.5 | 5.54 | - | | 1000 | 6.40 | 1.2 | 2.8691 | 50.6 |
| Run# 142 7/11/96 | 120 | 662 | 7.00 | 21.8 | 5.54 | - | | 1000 | 6.40 | 1.2 | 2.4008 | 57.1 |
| Run #149 8/96 | 60 | 662 | 4.47 | 21.8 | 5.54 | - | | 975 | 7.15 | 2.1 | 2.1338 | 41.2 |
| Run #150 8/96 | 60 | 662 | 5.00 | 21.8 | 5.54 | - | | 775 | 8.00 | 2.1 | 2.4008 | 40.9 |
| Glenharold Mine Lignite | | | | | | | | | | | | |
| Run #153 (7/24/96) | 60 | 662 | 5.15 | 11.80 | 9.48 | 1.75 | - | - | 990 | 2.4 | 1.7166 | 68.7 |
| Run #155 (7/29/96) | 60 | 662 | 6.34 | 12.10 | 9.48 | 2.15 | - | - | 875 | 1.5 | 2.1953 | 67.0 |
| Run #156 (7/29/96) | 60 | 662 | 6.34 | 12.10 | 9.48 | 2.15 | 2.88 | 2.88 | 1260 | 1.5 | 1.7291 | 76.2 |
| Freedom Mine Lignite | | | | | | | | | | | | |
| Run #151 (7/24/96) | 60 | 662 | 5.00 | 28.70 | 4.46 | 1.75 | - | - | 775 | 2.2 | 1.7495 | 53.3 |
| Run #154 (7/26/96) | 60 | 662 | 5.00 | 28.20 | 4.46 | 2.15 | - | - | 1310 | 1.4 | 1.7165 | 54.6 |
| Run #158 (7/30/96) | 60 | 662 | 5.00 | 28.70 | 4.46 | 2.15 | 4.16 | 4.16 | 1490 | 1.4 | 0.9208 | 77.6 |
| Ohio 11 Mine Bituminous Coal | | | | | | | | | | | | |
| Run #152 (7/29/96) | 60 | 662 | 5.00 | 3.90 | 6.88 | - | - | - | 850 | 1.5 | 2.2790 | 56.5 |
| Run #157 (7/30/96) | 60 | 662 | 5.00 | 3.90 | 6.88 | - | 3.00 | 2.53 | 925 | 1.5 | 1.6673 | 70.2 |

# APPENDIX 2

## ONE-LITER AUTOCLAVE TESTS

## Table A2 -1

## One-Liter Autoclave Tests, Task 2

| Run No. | Charge | | | | | | Reaction Temp, °C | Residence Time, min | HI"A"/ dry Coal, g/g | Solvent/ dry Coal, g/g | System Pressure[f], psia | Coal Conversion, wt % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Coal Type[a] | Coal, g | Solvent[b] | Solvent, g | HI"A", g | Water, g | | | | | | |
| 2-LA | BT | 100 | D | 160.3 | 79.9 | - | 400 | 45 | 1.0 | 2.0 | 2650 | N/A |
| 3-LA | BT | 100 | D | 123.1 | 80.1 | - | 400 | 45 | 1.0 | 1.5 | 2675 | N/A |
| 4-LA | BT | 100 | D | 120.5 | 80.1 | - | 400 | 45 | 1. | 1.5 | 2675 | 84.0 |
| 4b-LA | BT | 100 | D | 121.7 | 80.5 | - | 400 | 45 | 1.0 | 1.5 | 2660 | 84.0[d] |
| 5-LA | BT | 100 | D | 120.2 | 80.3 | - | 350 | 150 | 1.0 | 1.5 | 2270 | 84.4 |
| 6-LA | O | 100 | D | 143.0 | 97.0 | - | 350 | 60 | 1.0 | 1.5 | 1870 | 88.8 |
| 7-LA | FM-HS | 94.2 | D | 202.3 | 124.9 | 30.6 | 350 | 60 | 1.0 | 2.5 | 3860 | 86.3 |
| 8-LA | GH | 103 | D | 220.4 | 92.2 | 35.6 | 350 | 60 | 1.0 | 2.4 | 2900 | 93.4[e] |
| 9-LA | GH | 103 | L | 220.2 | 92.2 | 34.8 | 350 | 60 | 1.0 | 2.4 | 2930 | 91.0 |
| 9a-LA | GH | 103 | L | 140.5 | 92.4 | 35.0 | 350 | 60 | 1.0 | 1.5 | 3000 | 93.0[e] |

a. Coals: BT - Black Thunder Mine Subbituminous
O - Ohio 11 Mine Bituminous
FM-HS - Freedom Mine Lignite, high sodium
GH - Glenharold Mine Lignite

b. Solvents: D - Wilsonville Run 262E V1074 distillate
L- Lummus Run 3LCF7 pasting solvent

c. Coal conversion to THF-solubles on $SO_3$- free ash-free basis; determined from ca. 10 g aliquots using ash balance methods

d. Determined by UK/CAER

e. Determined from THF-filtration of entire product

f. Maximum pressure recorded at reaction temperature

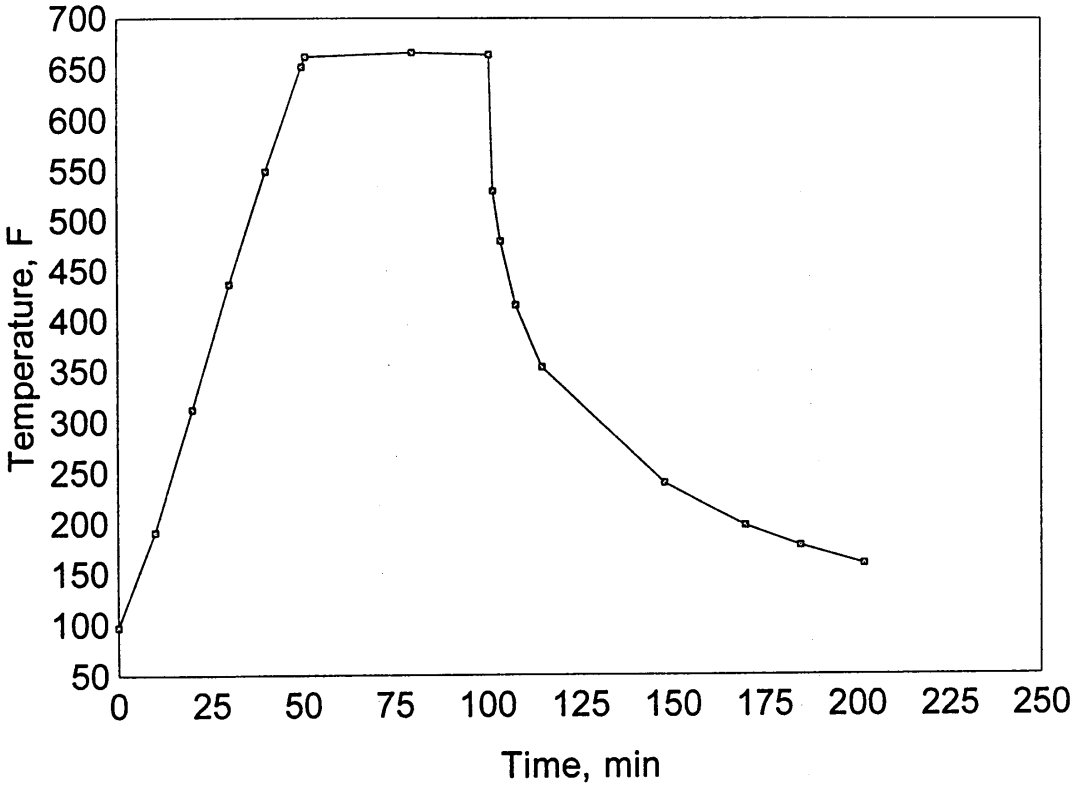



Figure A2-1. Heating and Cooling Profile, Typical One-Liter Autoclave Test.

# APPENDIX 3

## COST ANALYSIS FOR FILTRATION OF FIRST-STAGE PRODUCT COMMERCIAL SCALE

| | |
|---|---|
| One ton coal (dry) gives | 4bbl oil |
| $5x10^6$ t/year coal gives | $20x10^6$ bbl/year (60,000 bbl/day) |
| Amount of filtrate approx. | $7.5x10^6$ t/year |
| At overall filtration rate | 100 kg/$m^2$/hr |
| i.e., | 900 ton/$m^2$/yr |
| Filter area needed | 8,200 $m^2$ |

Allowing 25% extra installed capacity (modules of 5 filters, one of which is spare) then total installed cost of filtration area as per fig A 1 is $\$50x10^6$ (1989 prices)

Assuming a return of 20% to allow for running costs, i.e., $\$10x10^6$/year =50¢/bbl.

Note: The British Coal Conceptual Commercial LSE plant had a filtration section as 2% of installed cost and a total processing cost of $20/bbl, i.e., 40¢/bbl for filtration.

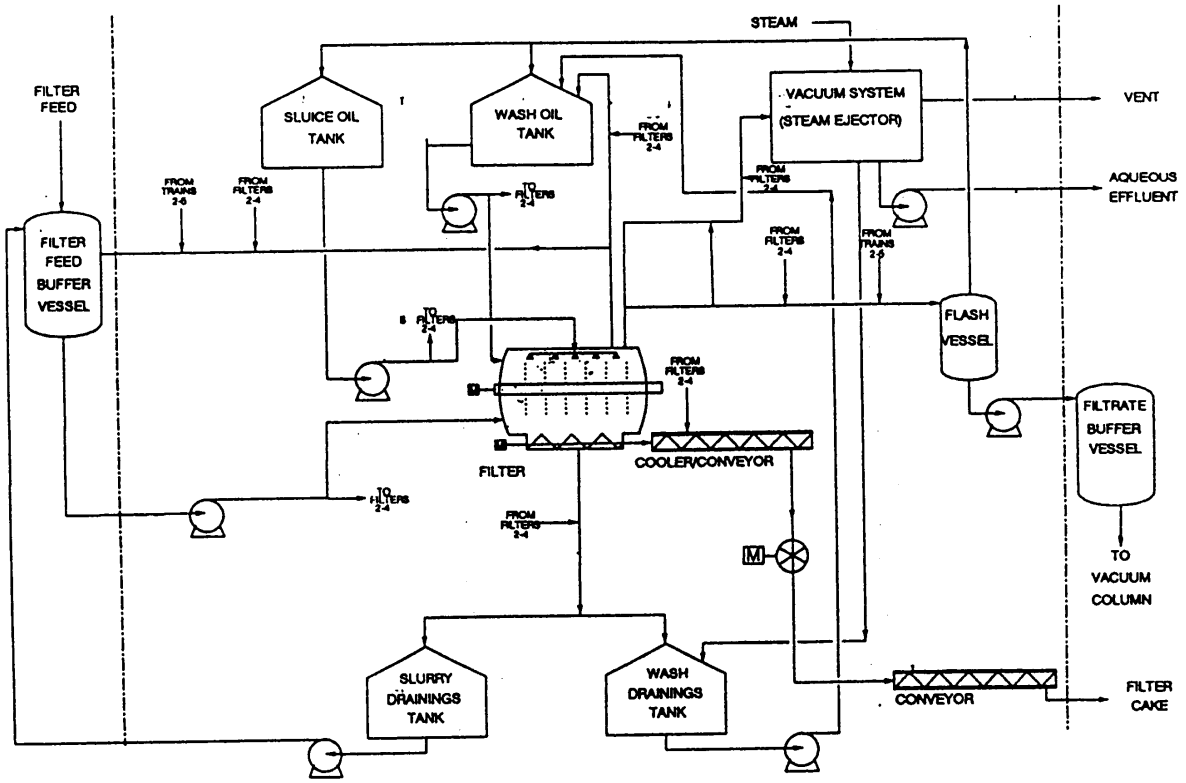



Figure A3-1. Commercial-Scale Filtration Process Flow Diagram.

# APPENDIX 4

## FILTRATION: THEORY and PRACTICE

## Filtration theory

The properties of a slurry that influences the rate of filtration are the viscosity of the fluid phase (i.e., of the filtrate) and the nature of the solids that form the filter cake. The overall resistance to the flow also includes a contribution from the filter screen itself. The above together with the filter area and the differential pressure (i.e., the driving force) are brought together for constant pressure filtration in the equation (1) below, which is based on Darcy's Law.[26]

$$\frac{1}{Rate} = \frac{dt}{dv} = \frac{\alpha \mu c v}{A^2 p} + \frac{\mu R}{Ap} \qquad (1)$$

Where the solids concentration $c$, the viscosity $\mu$, and the cake resistivity $\alpha$, are properties of the slurry, the area $A$ and the resistance of the medium $R$ are properties of the filter and $p$ is the applied pressure across the filter.

Following integration and insertion of boundary conditions:

$$\frac{t-t_o}{v-v_o} = \frac{\alpha \mu c (v+v_o)}{2A^2 p} + \frac{\mu R}{Ap} \qquad (2)$$

Plotting $(t - t_0)/(v - v_0)$ against $(v + v_0)$ gives a straight line of slope, $m$, and intercept $b$.
Thus:

$$\alpha = \frac{2A^2 mp}{\mu c} \qquad (3)$$

$$R = \frac{bAp}{\mu} \qquad (4)$$

Determination of the cake resistivity $\alpha$ and the fluid viscosity $\mu$ effectively define the filtration characteristics of the slurry.

(i) Effect of filtrate viscosity on filtration rate
The relationship between temperature, $\Theta$, and viscosity $\mu$, for Newtonian fluids is of the general form:

$$\mu = Be^{-E/\Theta} \qquad (5)$$

Where *B* and *E* are characteristic constants of the fluid. In practice, the viscosity of coal solutions deviate somewhat from the ideal and viscosities of coal solutions are usually measured at a temperature as close to the filtration temperature as possible. The fact that the rate of filtration is inversely proportional to the fluid viscosity and the form of the temperature viscosity relationship imply that the filtration needs to be performed at as high a temperature as possible. In practice other factors generally limit the upper temperature at which filters operate, (e.g., vaporization of the coal solution) and in addition the exponential term means that for most coal solutions there is little benefit to be gained from a marginally lower viscosity as the temperature is raised above about 300 °C.

Other parameters, e.g., coal to solvent ratio, solvent type and digestion conditions (temperature and time) may have a smaller effect upon the viscosity of the coal solution. However, their values are generally selected to optimize other process considerations such as product yields and process costs and are not therefore, generally considered as a means of controlling fluid viscosity.

(ii) Effect of filtration conditions on cake resistivity

For many coal digests the cake resistivity is a function of filtration temperature. This is apparent from the observation that the filtration rate does not increase with increasing temperature as much as would be expected from the known decrease in fluid viscosity. However, for digests from coals with very high mineral matter content and for slurries of anthracite in coal slurries[30] the rates were observed to increase in the expected manner. It may be concluded that the cake resistivity increases with temperature due to the changing properties of the coal residue particles.[26]

Filter cakes produced from coal digests have also been shown to be compressible, i.e., the cake resistivity increases with increasing pressure according to equation (6).

$$\alpha = \alpha_o p^n \qquad (6)$$

Where $\alpha_0$ is a constant and $n$ the compressibility coefficient, normally falling in the range 0.3 and 0.7. Anthracite slurries again show near ideal behavior with $n$ close to zero, i.e., anthracite particles pack in the same way regardless of temperature and pressure.[26]

It also has been observed[26] that cakes are less compressible as the temperature increases, presumably because the increase in temperature has already caused closer packing and there is therefore less scope for pressure to further reduce voidage.

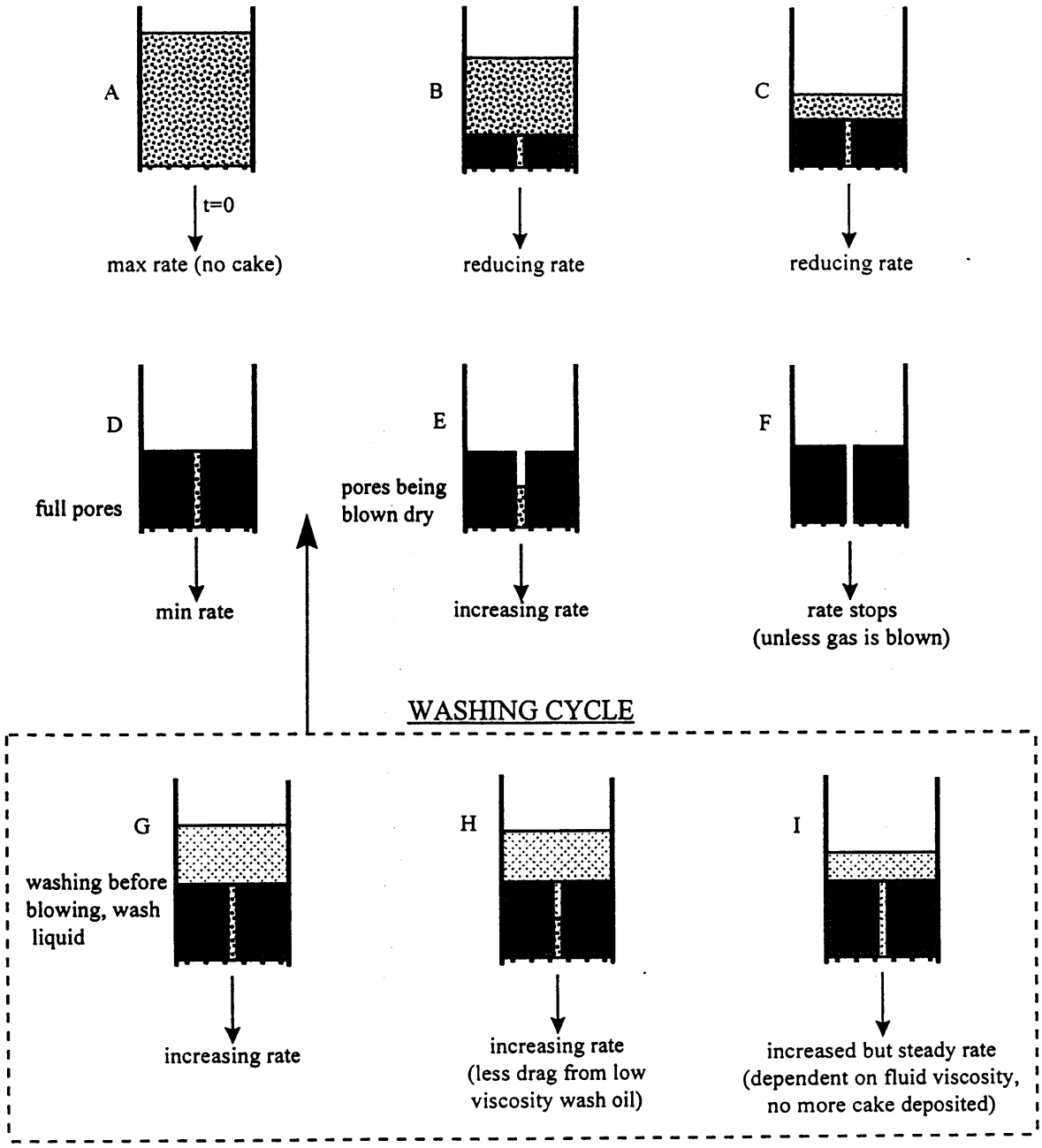
## 3.2 Filtration in Practice

Fig. A4-1 shows the progression through an idealized filtration cycle, including later processing of the filter cake to recover valuable product. At (A) before bridging of the screen has occurred, the flow rate will be limited only by the resistance to flow of the filter medium and associated pipe work and by the viscosity of the slurry; the solids are uniformly dispersed throughout the slurry and the flow rate will be at its maximum value. Once bridging of the screen apertures has occurred, the cake builds in thickness as particles are continuously added to it, the increasing resistance to flow resulting in a reduced flow rate, (B + C). At D the last of the solids has been deposited and liquid fills the void space in the cake, the flow rate is at its minimum value. Once gas starts to displace the liquid from the pores in the cake, (E), the resistance to flow should fall with a resulting increase in apparent flow rate from the unit, until eventually gas breakthrough occurs and the rate falls to zero (F). If cake washing is undertaken (G), then for maximum cycle

efficiency this is ideally initiated at time (D). As the lighter wash solvent displaces the coal solution in the cake pores (H), the filtration rate increases slightly as a consequence of its lower viscosity. When all of the coal solution has been displaced by wash solvent (I), the flow rate will stabilize at its higher rate. Vacuum drying can then be used to recover the distillable solvent contained in the cake. A dry cake is then discharged from the filter.

For rigid particulates uniformly dispersed throughout a viscous fluid, the filtration rate data will follow the classic form predicted by Darcy's equation. The flow rate will diminish as the cake thickness builds and the resistance to flow increases. However, for many of the coal digests found here, some of the solute readily precipitates from solution, the amount varying with temperature and time. This can result in agglomeration and rapid settling within the filter, and in consequence filtration proceeds with a much more mobile fluid phase, depleted in solids, passing through the cake. In this case, the filtration rate will be approximately constant as flow continues, since the cake is not changing with time; (in practice, subtle changes may occur as material in the cake may redissolve or perhaps, more may precipitate from solution, depending upon spatial and temporal temperature variations in the filter). An approximate evaluation of cake resistivity can then be made from the mean flow rate, through a simplification of Darcy's equation.

Acquisition of reliable filtration data is difficult on the micro scale attempted here. For example, the measures taken to mitigate settling of the solids in the filter during the warm-up period, were not particularly effective. Other factors fundamental to the scale of the operation include the fact that filtration is essentially a random, collective process where large numbers of data points greatly assist interpretation of the data. For some of the materials tested here the high viscosity of the fluids produces hold-up in the filter outlet and a large liquid drop size - significant in size in relation to the total volume of filtrate. However, it was originally anticipated that the information obtainable from these tests would simply provide an answer to the question of whether filtration was a feasible option for these materials. In the event, this was more than accomplished although improved data can be expected as the scale of the tests is increased, while still under laboratory conditions.




Note: Single pore is diagrammatic of all cake porosity through which fluid flows

Figure A4-1. Idealized Filtration Sequence.

# APPENDIX 2

## ONE-LITER AUTOCLAVE TESTS

## Table A2 -1

## One-Liter Autoclave Tests, Task 2

| Run No. | Charge | | | | | | Reaction Temp, °C | Residence Time, min | HI"A"/ dry Coal, g/g | Solvent/ dry Coal, g/g | System Pressure[f], psia | Coal Conversion, wt % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Coal Type[a] | Coal, g | Solvent[b] | Solvent, g | HI"A", g | Water, g | | | | | | |
| 2-LA | BT | 100 | D | 160.3 | 79.9 | - | 400 | 45 | 1.0 | 2.0 | 2650 | N/A |
| 3-LA | BT | 100 | D | 123.1 | 80.1 | - | 400 | 45 | 1.0 | 1.5 | 2675 | N/A |
| 4-LA | BT | 100 | D | 120.5 | 80.1 | - | 400 | 45 | 1. | 1.5 | 2675 | 84.0 |
| 4b-LA | BT | 100 | D | 121.7 | 80.5 | - | 400 | 45 | 1.0 | 1.5 | 2660 | 84.0[d] |
| 5-LA | BT | 100 | D | 120.2 | 80.3 | - | 350 | 150 | 1.0 | 1.5 | 2270 | 84.4 |
| 6-LA | O | 100 | D | 143.0 | 97.0 | - | 350 | 60 | 1.0 | 1.5 | 1870 | 88.8 |
| 7-LA | FM-HS | 94.2 | D | 202.3 | 124.9 | 30.6 | 350 | 60 | 1.0 | 2.5 | 3860 | 86.3 |
| 8-LA | GH | 103 | D | 220.4 | 92.2 | 35.6 | 350 | 60 | 1.0 | 2.4 | 2900 | 93.4[e] |
| 9-LA | GH | 103 | L | 220.2 | 92.2 | 34.8 | 350 | 60 | 1.0 | 2.4 | 2930 | 91.0 |
| 9a-LA | GH | 103 | L | 140.5 | 92.4 | 35.0 | 350 | 60 | 1.0 | 1.5 | 3000 | 93.0[e] |

a. Coals: BT - Black Thunder Mine Subbituminous
O - Ohio 11 Mine Bituminous
FM-HS - Freedom Mine Lignite, high sodium
GH - Glenharold Mine Lignite

b. Solvents: D - Wilsonville Run 262E V1074 distillate
L- Lummus Run 3LCF7 pasting solvent

c. Coal conversion to THF-solubles on $SO_3$- free ash-free basis; determined from ca. 10 g aliquots using ash balance methods

d. Determined by UK/CAER

e. Determined from THF-filtration of entire product

f. Maximum pressure recorded at reaction temperature

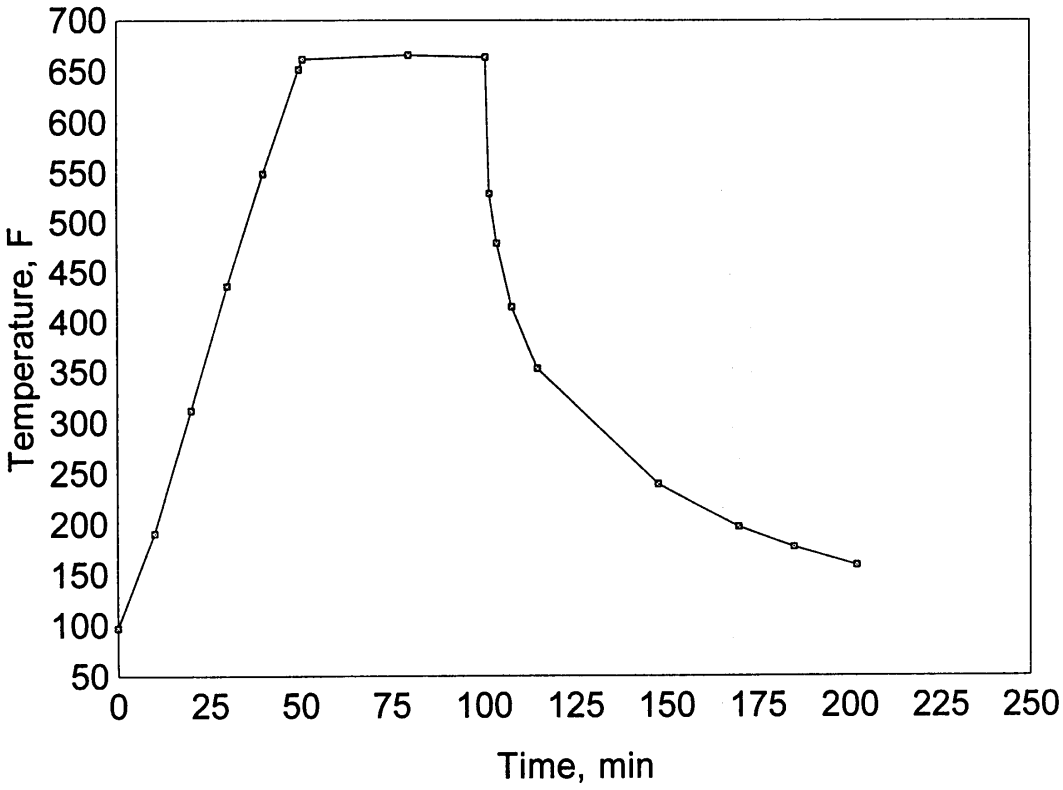



Figure A2-1. Heating and Cooling Profile, Typical One-Liter Autoclave Test.

# APPENDIX 3

## COST ANALYSIS FOR FILTRATION OF FIRST-STAGE PRODUCT COMMERCIAL SCALE

| | |
|---|---|
| One ton coal (dry) gives | 4bbl oil |
| $5x10^6$ t/year coal gives | $20x10^6$ bbl/year (60,000 bbl/day) |
| Amount of filtrate approx. | $7.5x10^6$ t/year |
| At overall filtration rate | 100 kg/$m^2$/hr |
| i.e., | 900 ton/$m^2$/yr |
| Filter area needed | 8,200 $m^2$ |

Allowing 25% extra installed capacity (modules of 5 filters, one of which is spare) then total installed cost of filtration area as per fig A 1 is $\$50x10^6$ (1989 prices)

Assuming a return of 20% to allow for running costs, i.e., $\$10x10^6$/year =50¢/bbl.

Note: The British Coal Conceptual Commercial LSE plant had a filtration section as 2% of installed cost and a total processing cost of $20/bbl, i.e., 40¢/bbl for filtration.

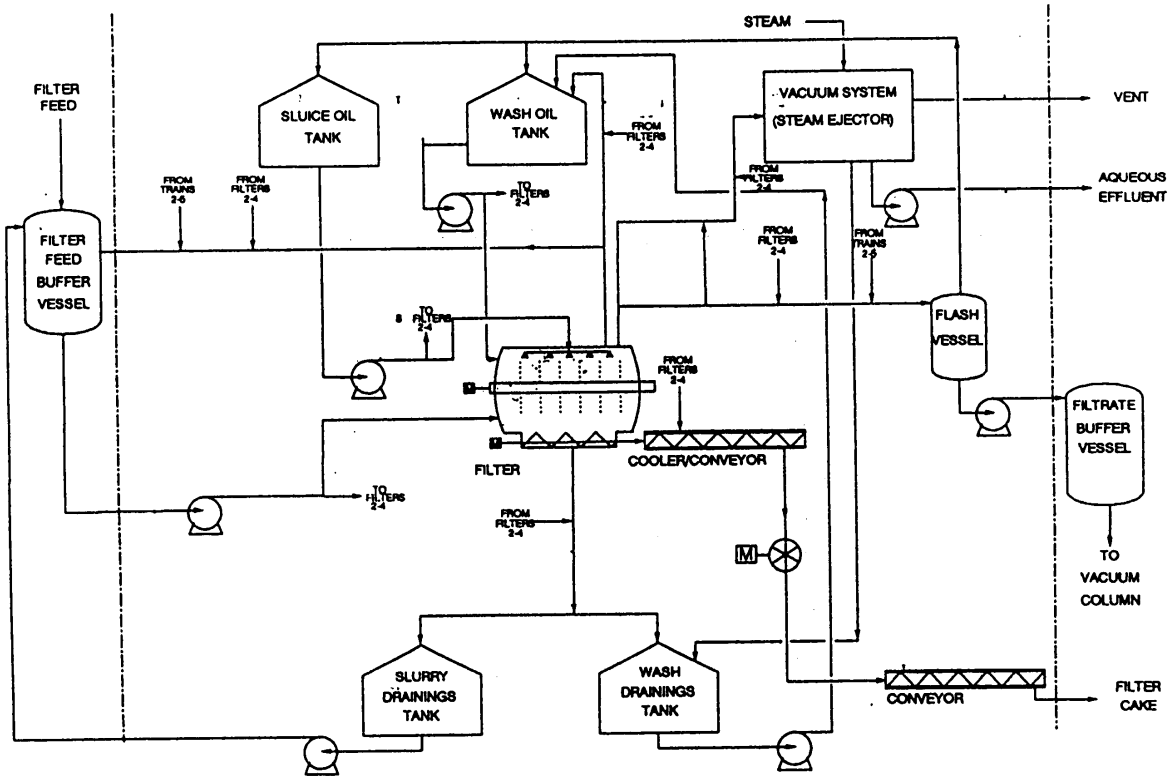



Figure A3-1. Commercial-Scale Filtration Process Flow Diagram.

# APPENDIX 4

## FILTRATION: THEORY and PRACTICE

## Filtration theory

The properties of a slurry that influences the rate of filtration are the viscosity of the fluid phase (i.e., of the filtrate) and the nature of the solids that form the filter cake. The overall resistance to the flow also includes a contribution from the filter screen itself. The above together with the filter area and the differential pressure (i.e., the driving force) are brought together for constant pressure filtration in the equation (1) below, which is based on Darcy's Law.[26]

$$\frac{1}{Rate} = \frac{dt}{dv} = \frac{\alpha \mu c v}{A^2 p} + \frac{\mu R}{Ap} \qquad (1)$$

Where the solids concentration $c$, the viscosity $\mu$, and the cake resistivity $\alpha$, are properties of the slurry, the area $A$ and the resistance of the medium $R$ are properties of the filter and $p$ is the applied pressure across the filter.

Following integration and insertion of boundary conditions:

$$\frac{t-t_o}{v-v_o} = \frac{\alpha \mu c (v+v_o)}{2A^2 p} + \frac{\mu R}{Ap} \qquad (2)$$

Plotting $(t - t_0)/(v - v_0)$ against $(v + v_0)$ gives a straight line of slope, $m$, and intercept $b$. Thus:

$$\alpha = \frac{2A^2 mp}{\mu c} \qquad (3)$$

$$R = \frac{bAp}{\mu} \qquad (4)$$

Determination of the cake resistivity $\alpha$ and the fluid viscosity $\mu$ effectively define the filtration characteristics of the slurry.

(i) Effect of filtrate viscosity on filtration rate

The relationship between temperature, $\Theta$, and viscosity $\mu$, for Newtonian fluids is of the general form:

$$\mu = Be^{-E/\Theta} \qquad (5)$$

Where *B* and *E* are characteristic constants of the fluid. In practice, the viscosity of coal solutions deviate somewhat from the ideal and viscosities of coal solutions are usually measured at a temperature as close to the filtration temperature as possible. The fact that the rate of filtration is inversely proportional to the fluid viscosity and the form of the temperature viscosity relationship imply that the filtration needs to be performed at as high a temperature as possible. In practice other factors generally limit the upper temperature at which filters operate, (e.g., vaporization of the coal solution) and in addition the exponential term means that for most coal solutions there is little benefit to be gained from a marginally lower viscosity as the temperature is raised above about 300 °C.

Other parameters, e.g., coal to solvent ratio, solvent type and digestion conditions (temperature and time) may have a smaller effect upon the viscosity of the coal solution. However, their values are generally selected to optimize other process considerations such as product yields and process costs and are not therefore, generally considered as a means of controlling fluid viscosity.

(ii) Effect of filtration conditions on cake resistivity

For many coal digests the cake resistivity is a function of filtration temperature. This is apparent from the observation that the filtration rate does not increase with increasing temperature as much as would be expected from the known decrease in fluid viscosity. However, for digests from coals with very high mineral matter content and for slurries of anthracite in coal slurries[30] the rates were observed to increase in the expected manner. It may be concluded that the cake resistivity increases with temperature due to the changing properties of the coal residue particles.[26]

Filter cakes produced from coal digests have also been shown to be compressible, i.e., the cake resistivity increases with increasing pressure according to equation (6).

$$\alpha = \alpha_o p^n \qquad (6)$$

Where $\alpha_0$ is a constant and *n* the compressibility coefficient, normally falling in the range 0.3 and 0.7. Anthracite slurries again show near ideal behavior with *n* close to zero, i.e., anthracite particles pack in the same way regardless of temperature and pressure.[26]

It also has been observed[26] that cakes are less compressible as the temperature increases, presumably because the increase in temperature has already caused closer packing and there is therefore less scope for pressure to further reduce voidage.

3.2 Filtration in Practice

Fig. A4-1 shows the progression through an idealized filtration cycle, including later processing of the filter cake to recover valuable product. At (A) before bridging of the screen has occurred, the flow rate will be limited only by the resistance to flow of the filter medium and associated pipe work and by the viscosity of the slurry; the solids are uniformly dispersed throughout the slurry and the flow rate will be at its maximum value. Once bridging of the screen apertures has occurred, the cake builds in thickness as particles are continuously added to it, the increasing resistance to flow resulting in a reduced flow rate, (B + C). At D the last of the solids has been deposited and liquid fills the void space in the cake, the flow rate is at its minimum value. Once gas starts to displace the liquid from the pores in the cake, (E), the resistance to flow should fall with a resulting increase in apparent flow rate from the unit, until eventually gas breakthrough occurs and the rate falls to zero (F). If cake washing is undertaken (G), then for maximum cycle

efficiency this is ideally initiated at time (D). As the lighter wash solvent displaces the coal solution in the cake pores (H), the filtration rate increases slightly as a consequence of its lower viscosity. When all of the coal solution has been displaced by wash solvent (I), the flow rate will stabilize at its higher rate. Vacuum drying can then be used to recover the distillable solvent contained in the cake. A dry cake is then discharged from the filter.

For rigid particulates uniformly dispersed throughout a viscous fluid, the filtration rate data will follow the classic form predicted by Darcy's equation. The flow rate will diminish as the cake thickness builds and the resistance to flow increases. However, for many of the coal digests found here, some of the solute readily precipitates from solution, the amount varying with temperature and time. This can result in agglomeration and rapid settling within the filter, and in consequence filtration proceeds with a much more mobile fluid phase, depleted in solids, passing through the cake. In this case, the filtration rate will be approximately constant as flow continues, since the cake is not changing with time; (in practice, subtle changes may occur as material in the cake may redissolve or perhaps, more may precipitate from solution, depending upon spatial and temporal temperature variations in the filter). An approximate evaluation of cake resistivity can then be made from the mean flow rate, through a simplification of Darcy's equation.

Acquisition of reliable filtration data is difficult on the micro scale attempted here. For example, the measures taken to mitigate settling of the solids in the filter during the warm-up period, were not particularly effective. Other factors fundamental to the scale of the operation include the fact that filtration is essentially a random, collective process where large numbers of data points greatly assist interpretation of the data. For some of the materials tested here the high viscosity of the fluids produces hold-up in the filter outlet and a large liquid drop size - significant in size in relation to the total volume of filtrate. However, it was originally anticipated that the information obtainable from these tests would simply provide an answer to the question of whether filtration was a feasible option for these materials. In the event, this was more than accomplished although improved data can be expected as the scale of the tests is increased, while still under laboratory conditions.